Urban sources of contaminants of emerging concern: what is getting into the Chesapeake Bay and how can we reduce that load

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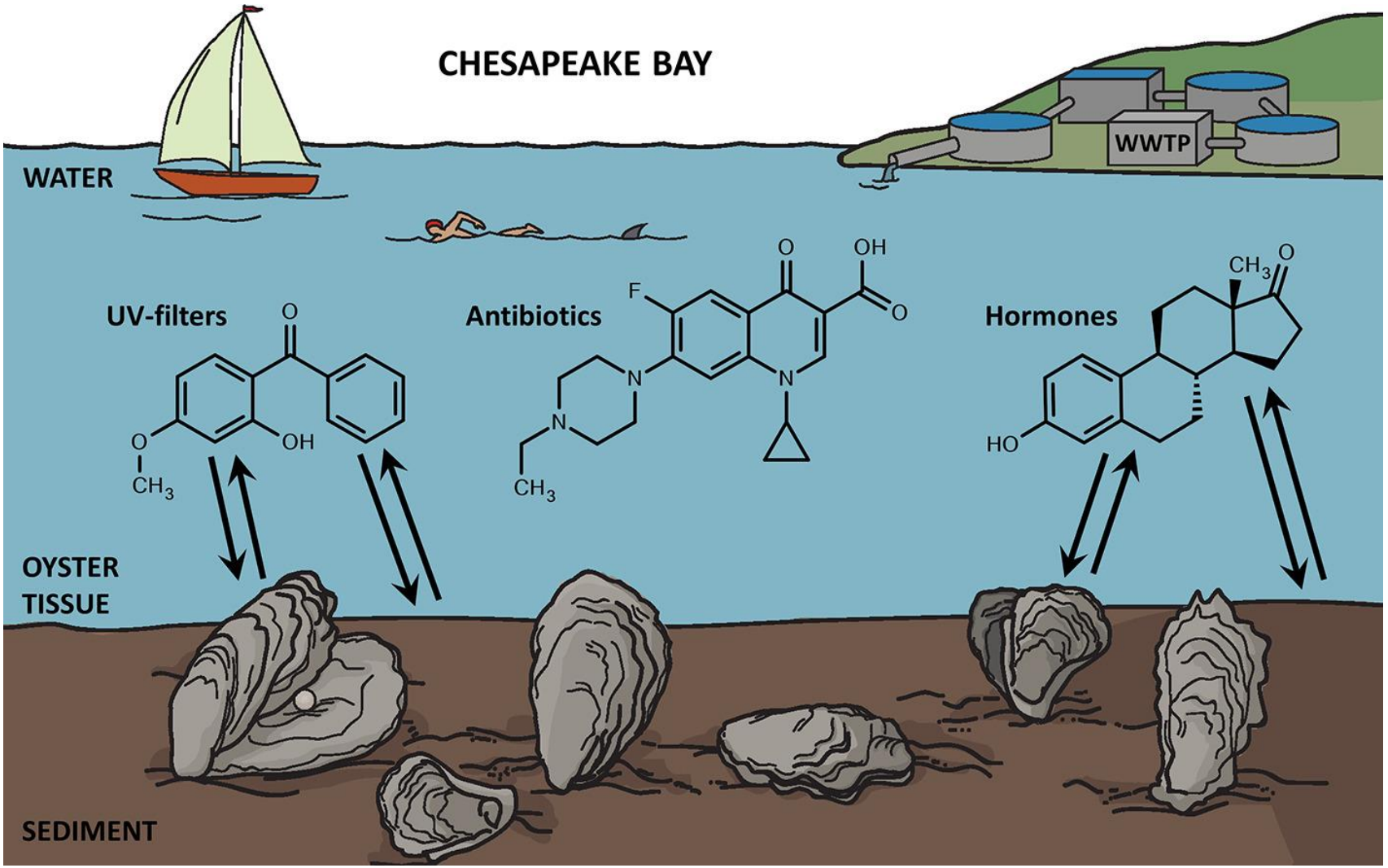
Chesapeake Bay Program, Integrating Science and Developing Approaches to Inform Management for Contaminants of Concern in Agricultural and Urban Settings Meeting (Baltimore, MD), May 22, 2019

Ultimately, the specialty chemicals that we use every day get discharged into the aquatic environment



My objectives for today's presentation

1. To measure antibiotics, hormones, and UV-filters in river systems discharging into the Chesapeake Bay and identify potential sources of these contaminants of emerging concern (CECs);

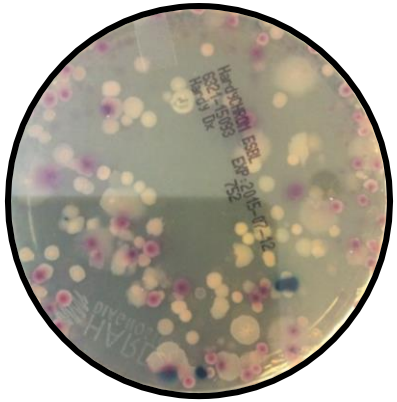
2. To determine whether antibiotics, hormones, and UV-filters are present in urban watersheds that do not receive effluent from wastewater treatment plants (WWTPs) or animal feeding operations (AFOs); and,

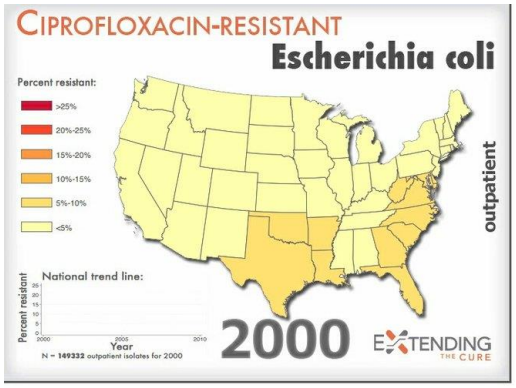
3. To describe removal mechanisms for antibiotics (and other CECs) in municipal WWTPs and discuss related challenges.

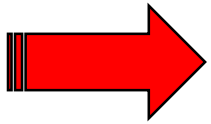
Contaminants of Emerging Concern (CECs)

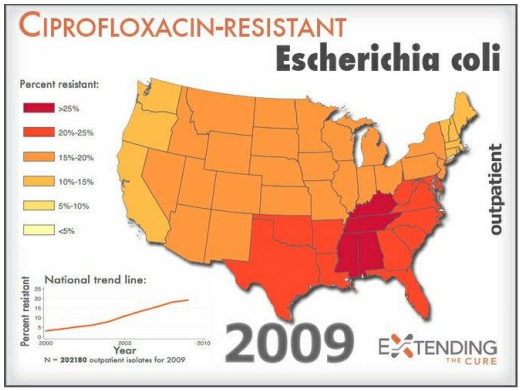
The environmental occurrence of antimicrobials has drastic & subtle implications for public & ecological health

Antimicrobial resistance is a global health challenge

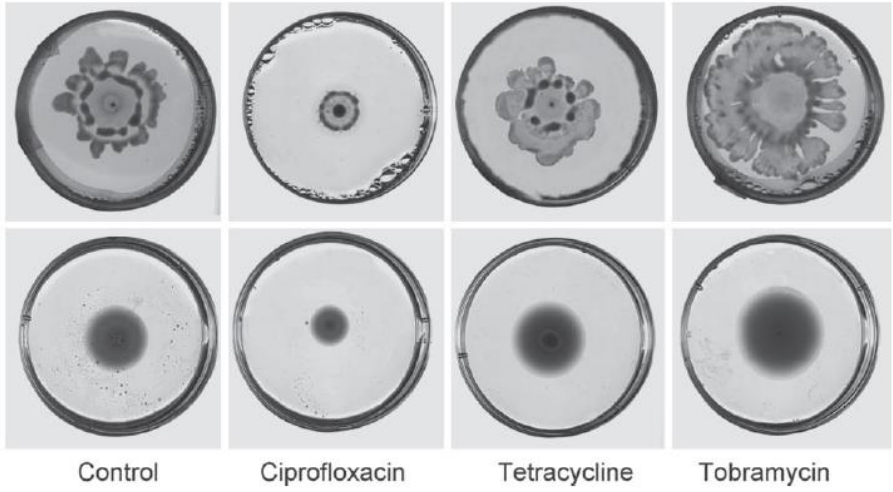






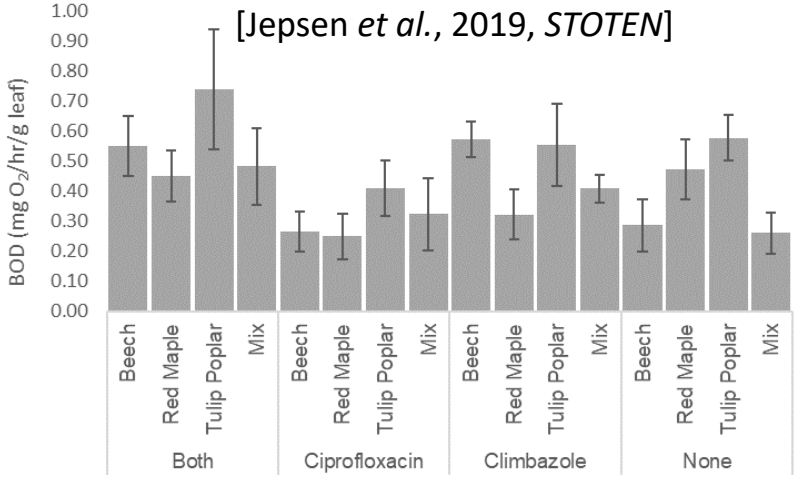


Effects on cell signaling [Linares *et al.*, 2006, *PNAS*]



Changes to carbon cycling

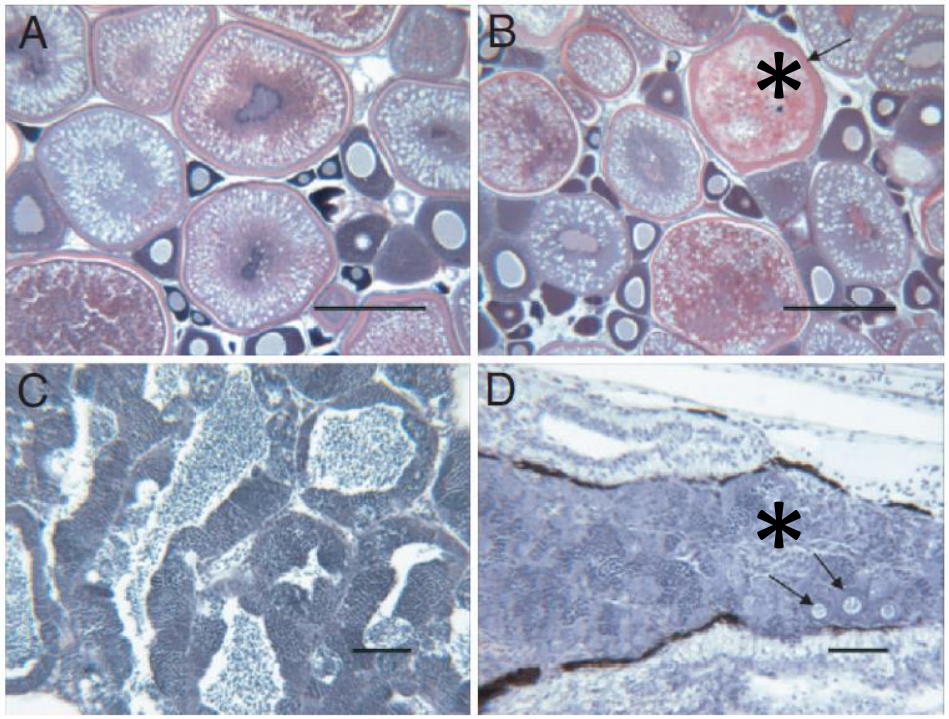
[Jepsen *et al.*, 2019, *STOTEN*]



Estrogenic hormones and other endocrine disrupting chemicals can severely disrupt ecosystems

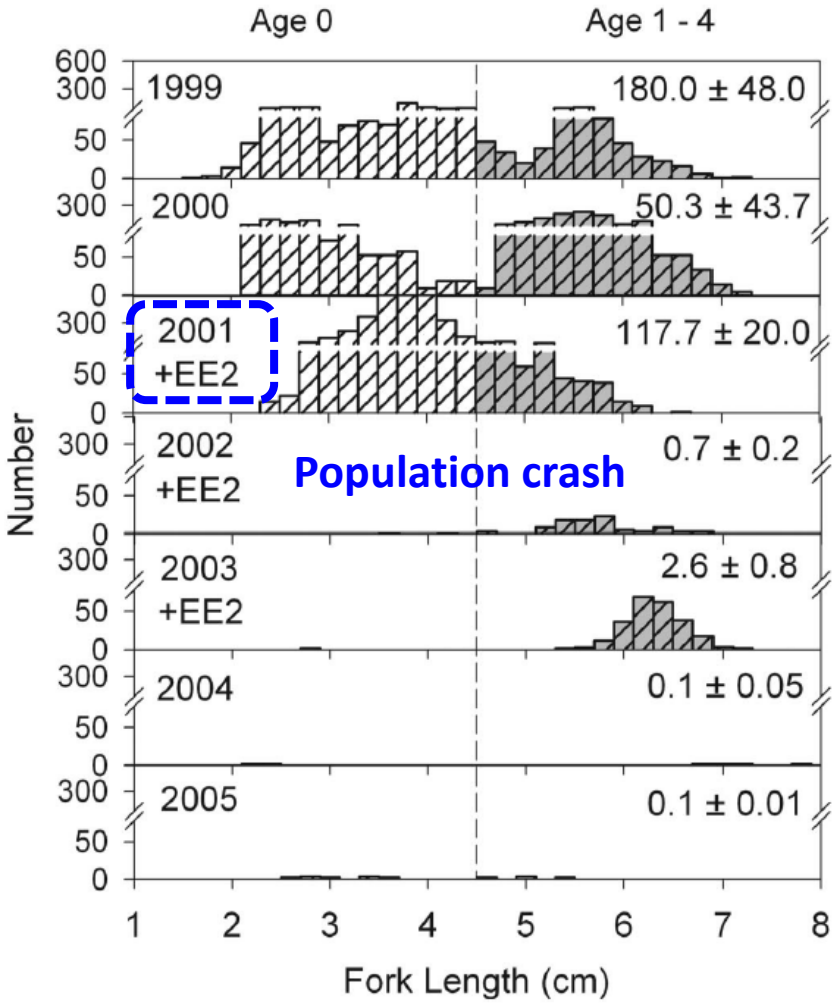
Reference lake

EE2-amended lake



B – Delayed ovarian development

D – Occurrence of intersex

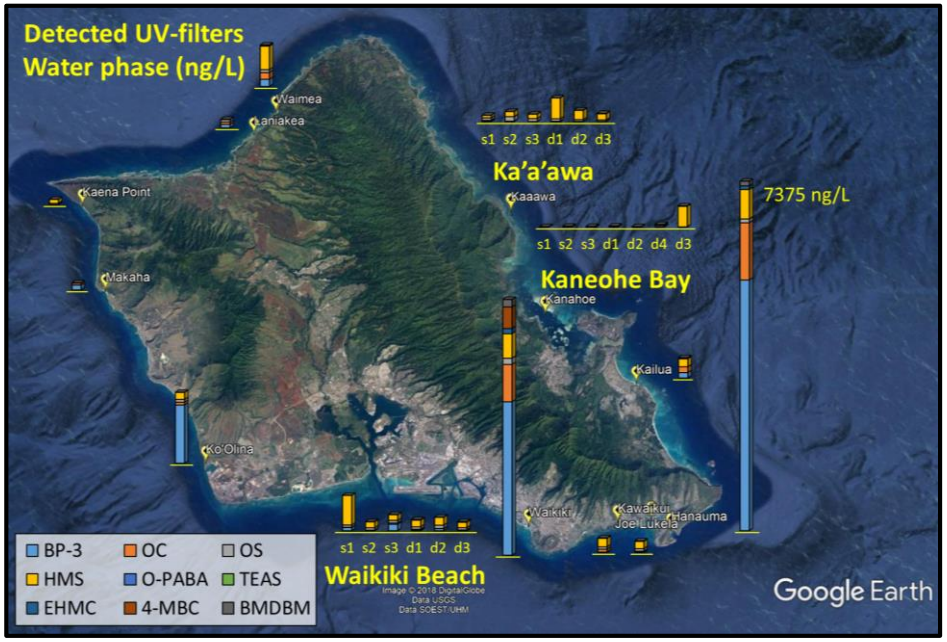


[Kidd *et al.*, 2007, *PNAS*]

UV-filters have been recently banned in Hawaii, Florida, & elsewhere due to coral toxicity concerns

"Oxybenzone poses a hazard to coral reef conservation and threatens the resiliency of coral reefs to climate change."

[Downs *et al.*, 2015, *Arch. Environ. Contam. Toxicol.*]

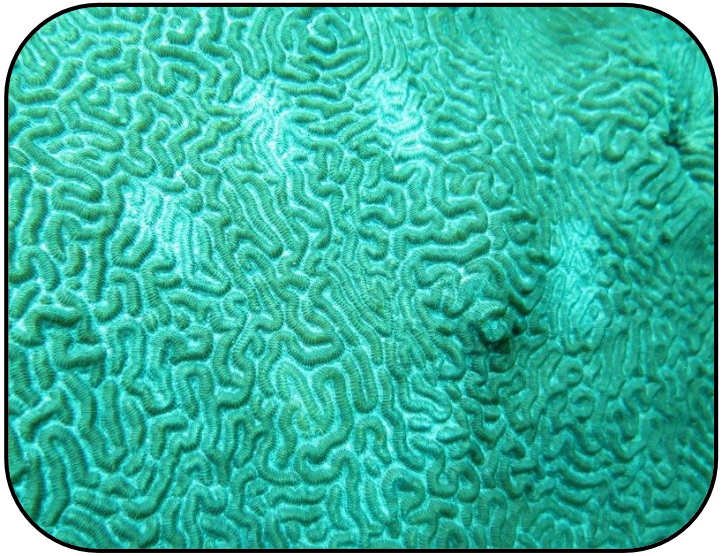


[Mitchelmore, He, *et al.*, 2019, *Sci. Total Environ.*]

The New York Times

Hawaii Passes Bill Banning Sunscreen That Can Harm Coral Reefs

The legislation prohibits the distribution of sunscreens containing chemicals that scientists have found contributes to coral bleaching when washed off in the ocean.



Analytical Methods

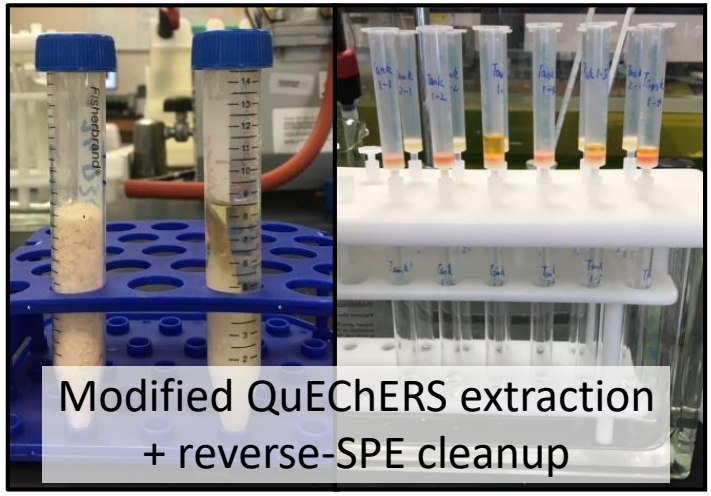
CEC extraction from water, sediment, and tissue helps to (1) concentrate analytes and (2) remove interferences

Water

Solid-phase extraction (SPE)

Tissue

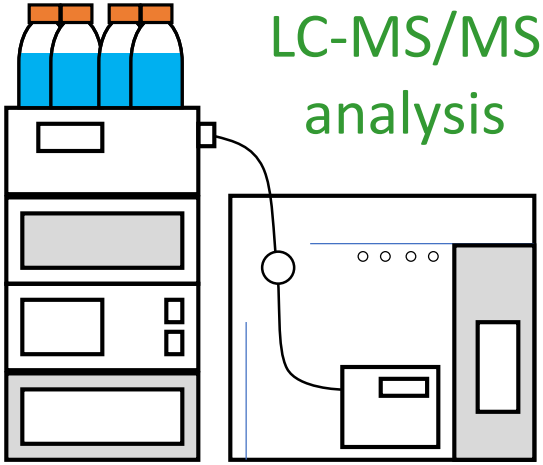
Sediment

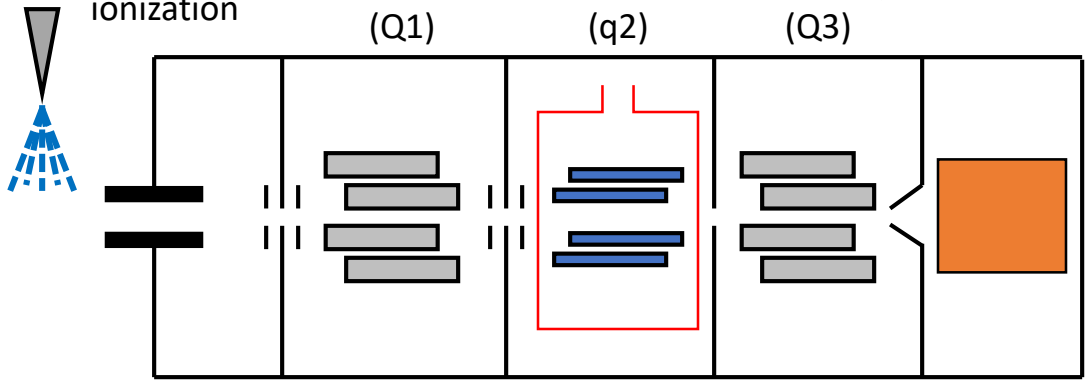


Modified QuEChERS extraction + reverse-SPE cleanup

extracts

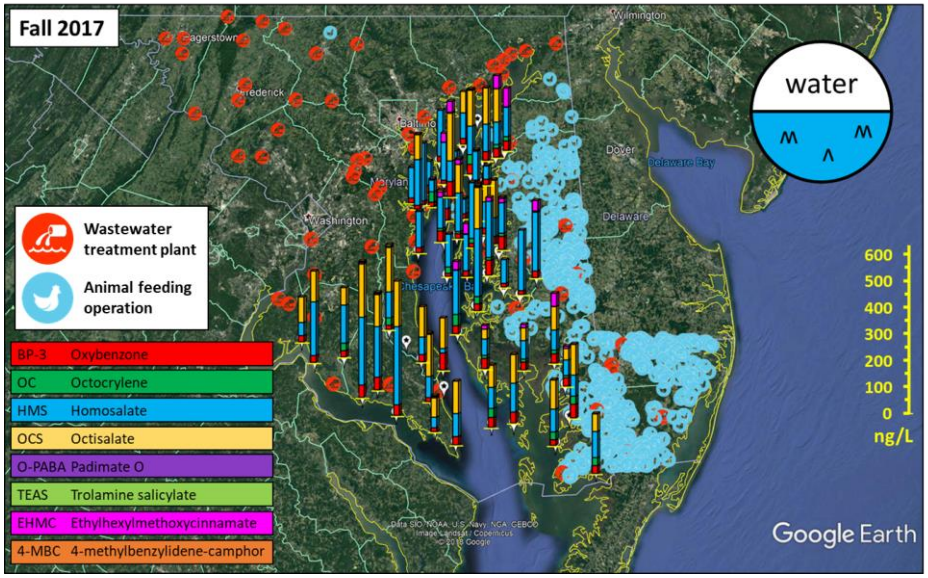
LC-MS/MS analysis





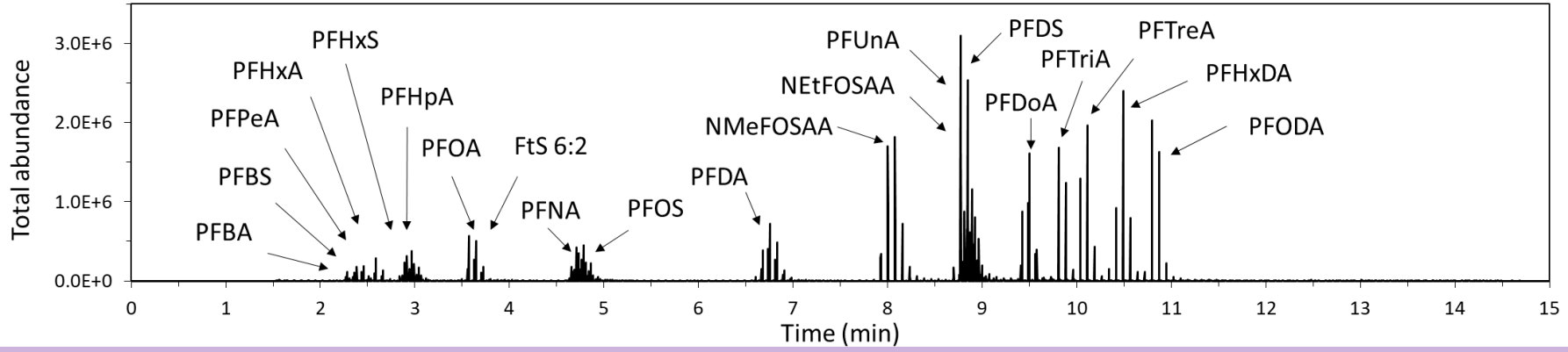
We have applied our LC-MS/MS-based methods to various sites, sample matrices, & chemicals

Antibiotics, hormones, UV-filters in Chesapeake Bay



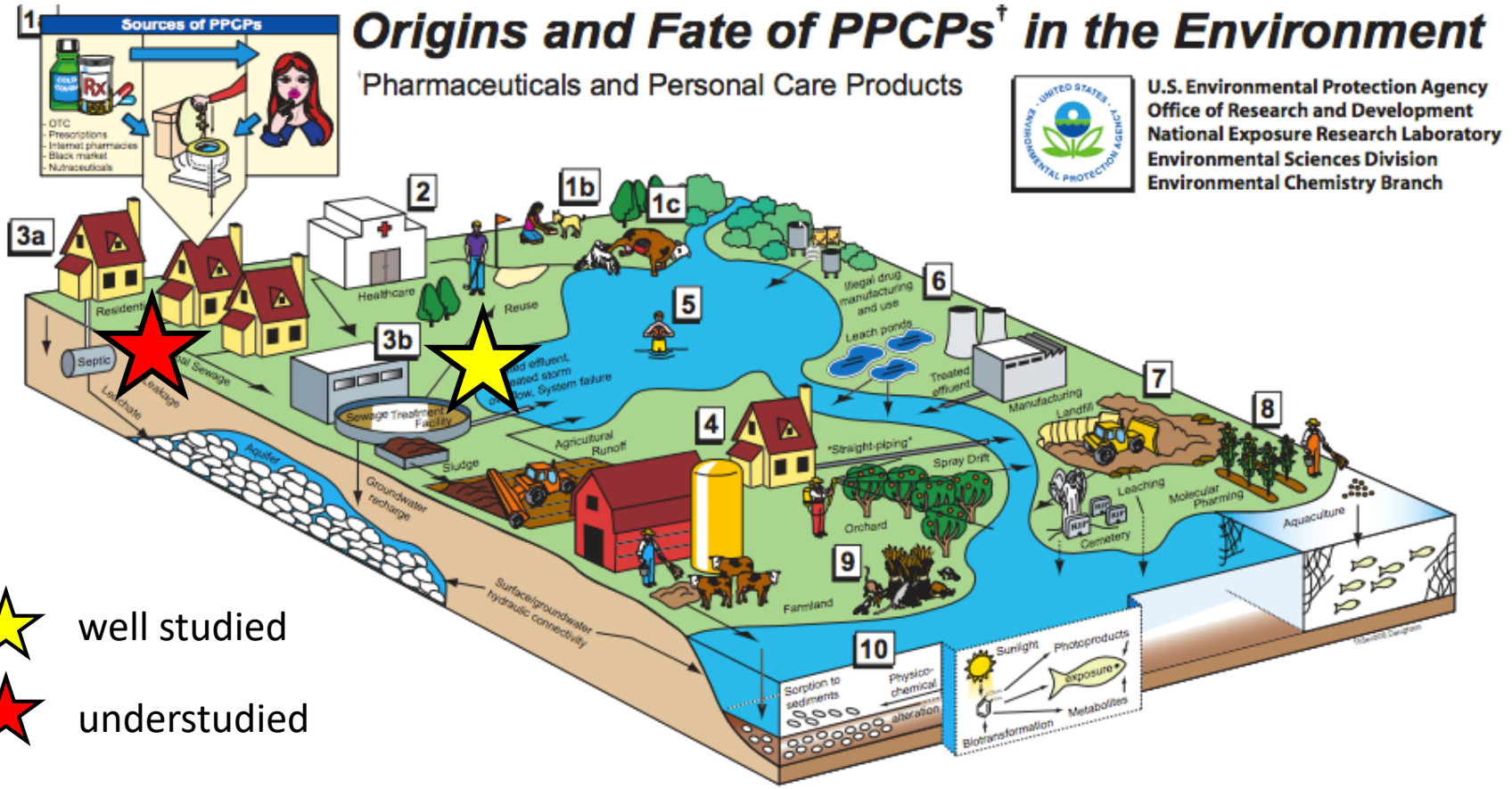
Hormones, UV-filters, & PFAS in organisms

Per- and polyfluoroalkyl substances (PFAS) in groundwater



CEC occurrence in urban systems

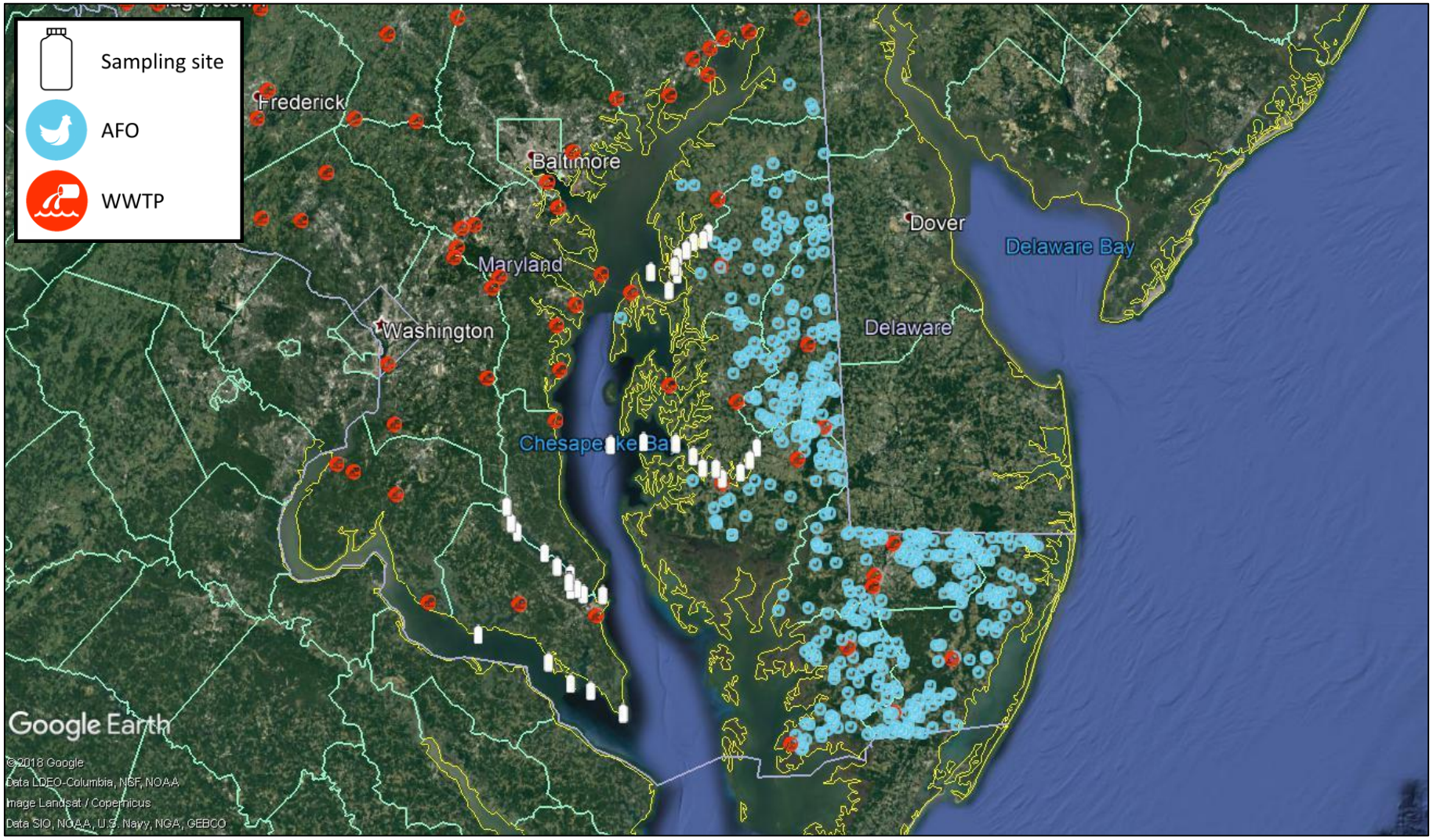
Urban sources of CECs into the environment have been assessed, but not (necessarily) well studied



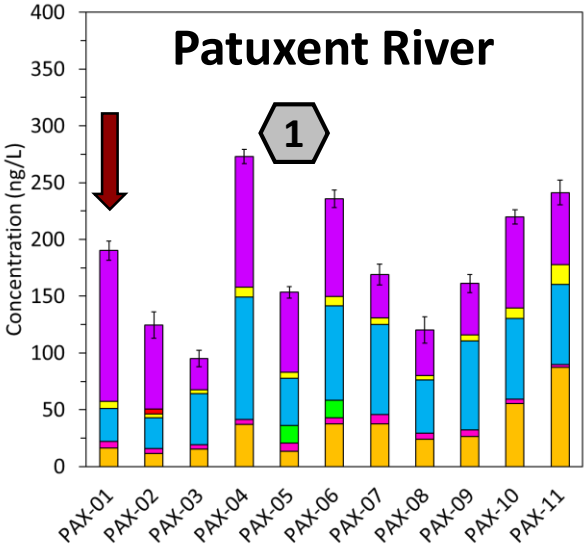
well studied

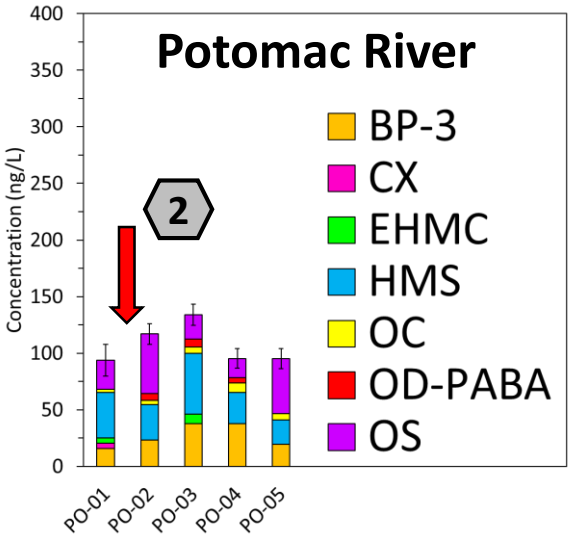
understudied

To explore CECs from urban sources, we collected samples from the Potomac, Patuxent, Choptank, and Chester rivers



The composition of detected UV-filters was similar in each river, but WWTP contributions were apparent

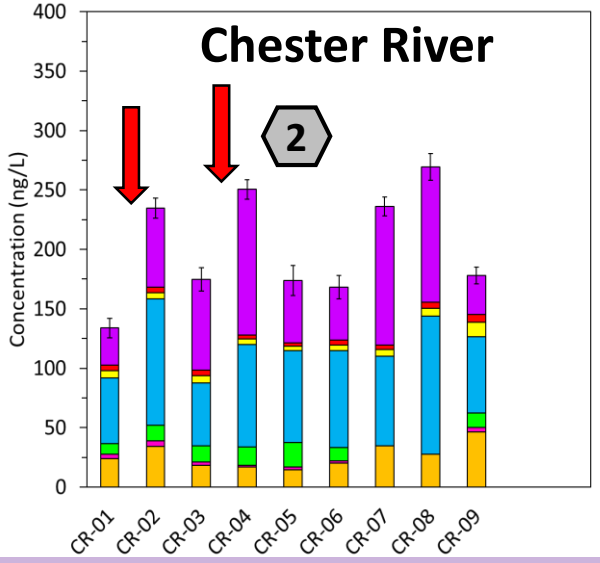


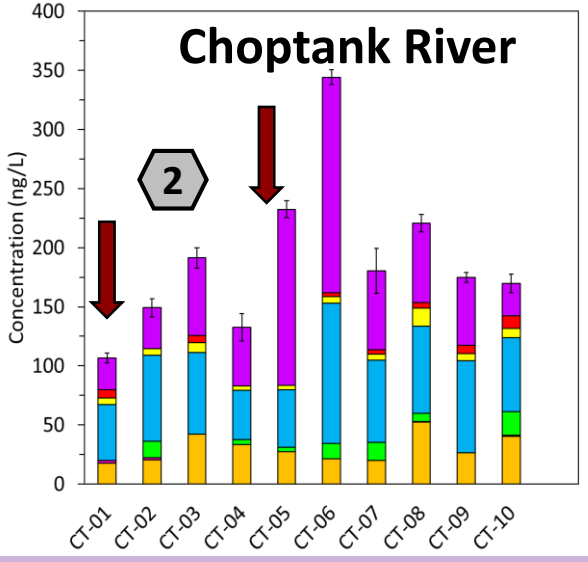


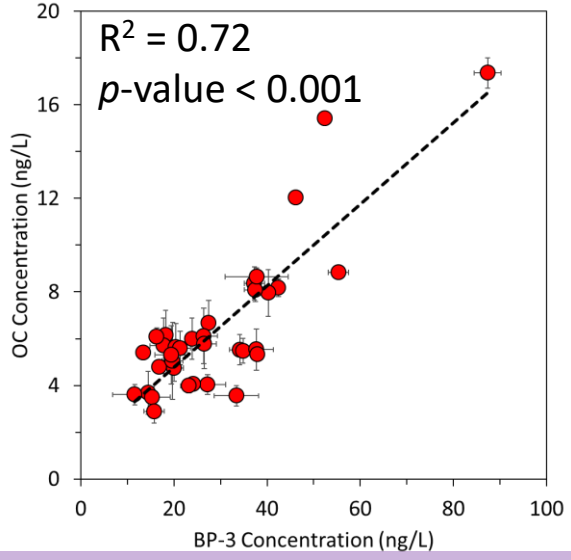
1 Higher concentrations downstream of marinas

2 Higher concentrations downstream of WWTPs

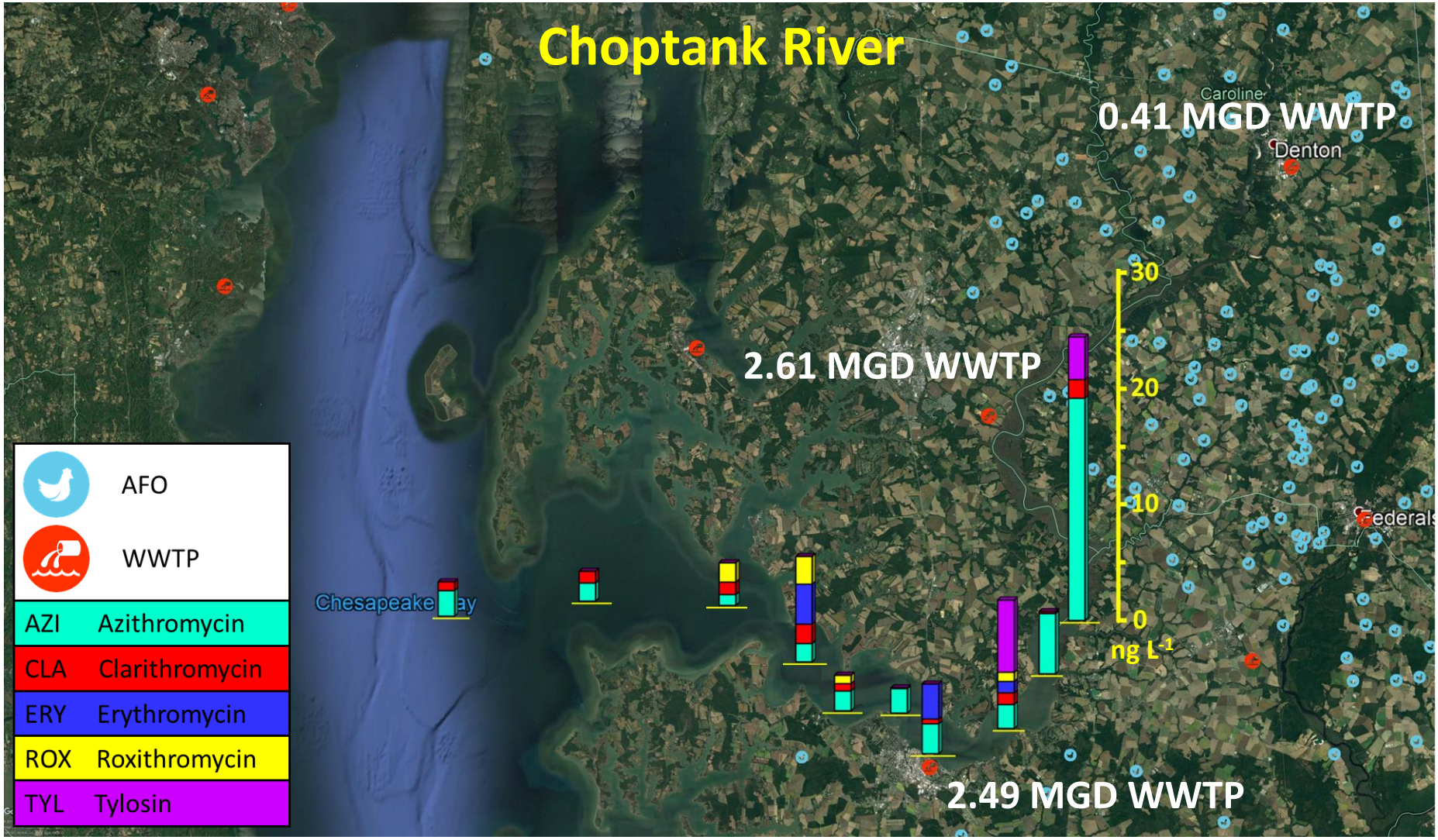
<1 MGD >1 MGD



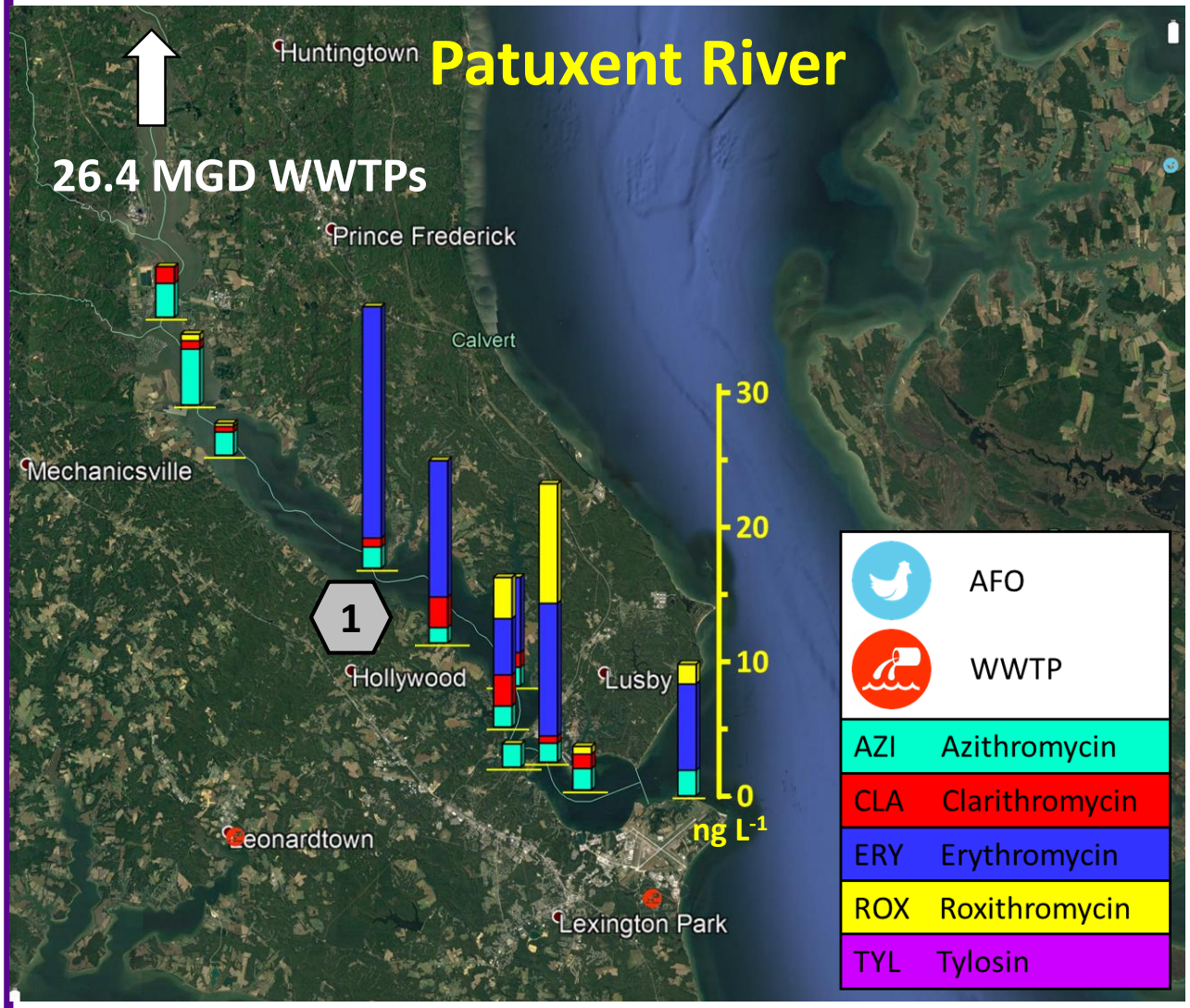




A variety of human- and animal-use macrolide antibiotics were detected in the Choptank River

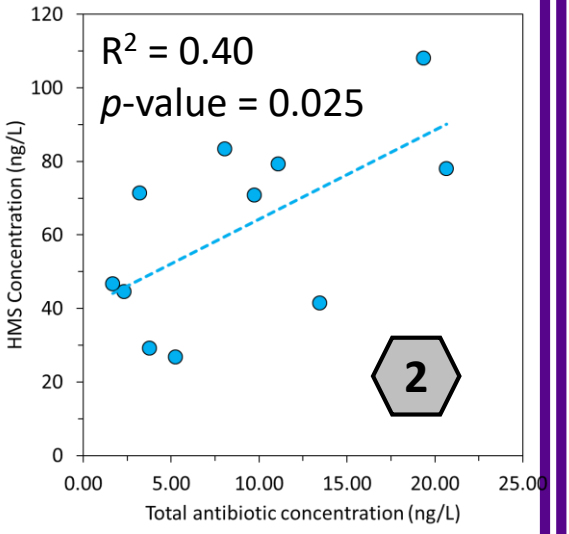


Similar detection trends were observed in the more urban Patuxent River, with high erythromycin levels

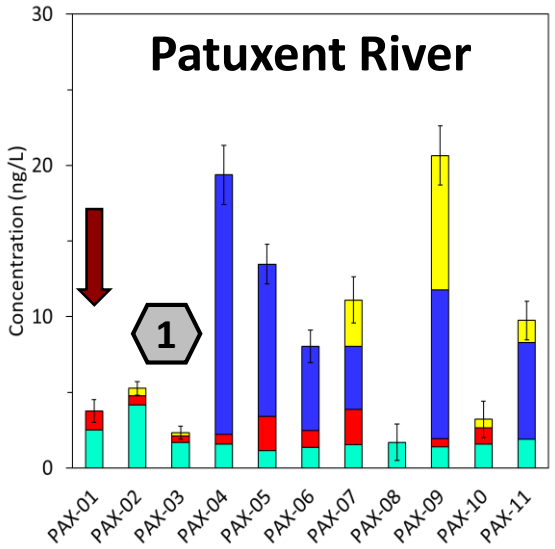


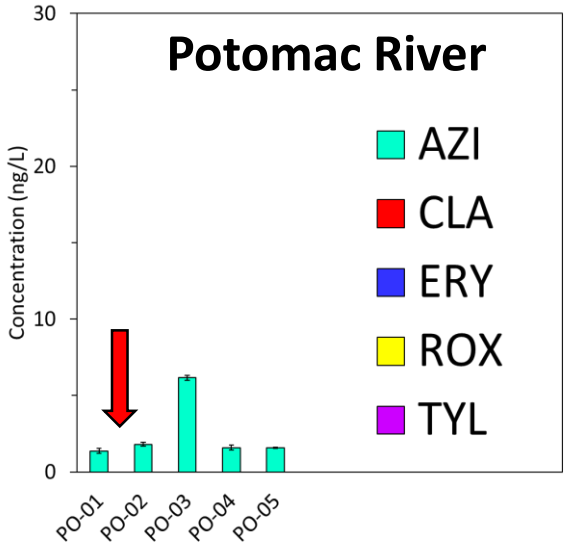
1. Macrolide levels increased at same locations as UV-filters.

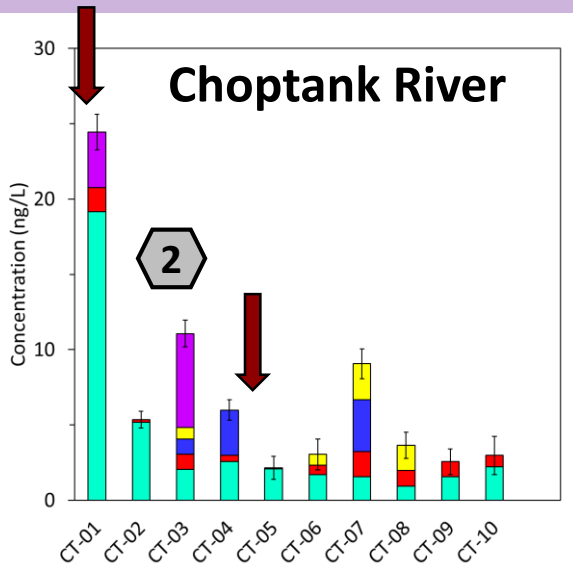
2. HMS positively correlated with the total concentration of antibiotics.

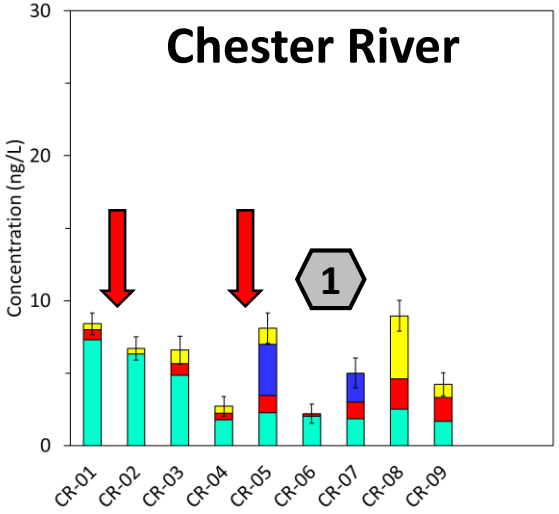


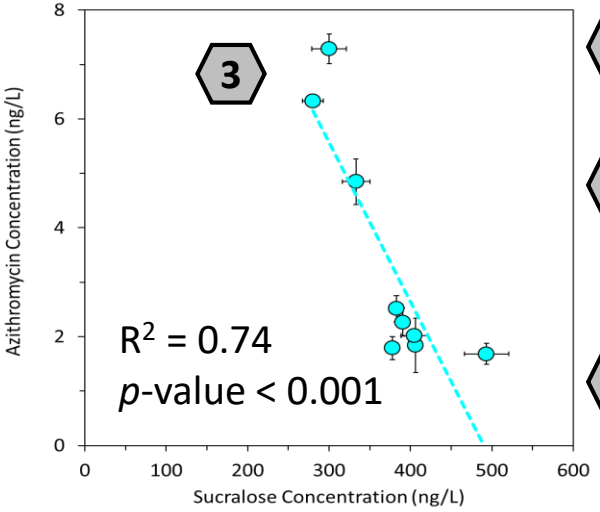
Antibiotic detections and levels suggested influence of WWTPs, AFOs, and active degradation









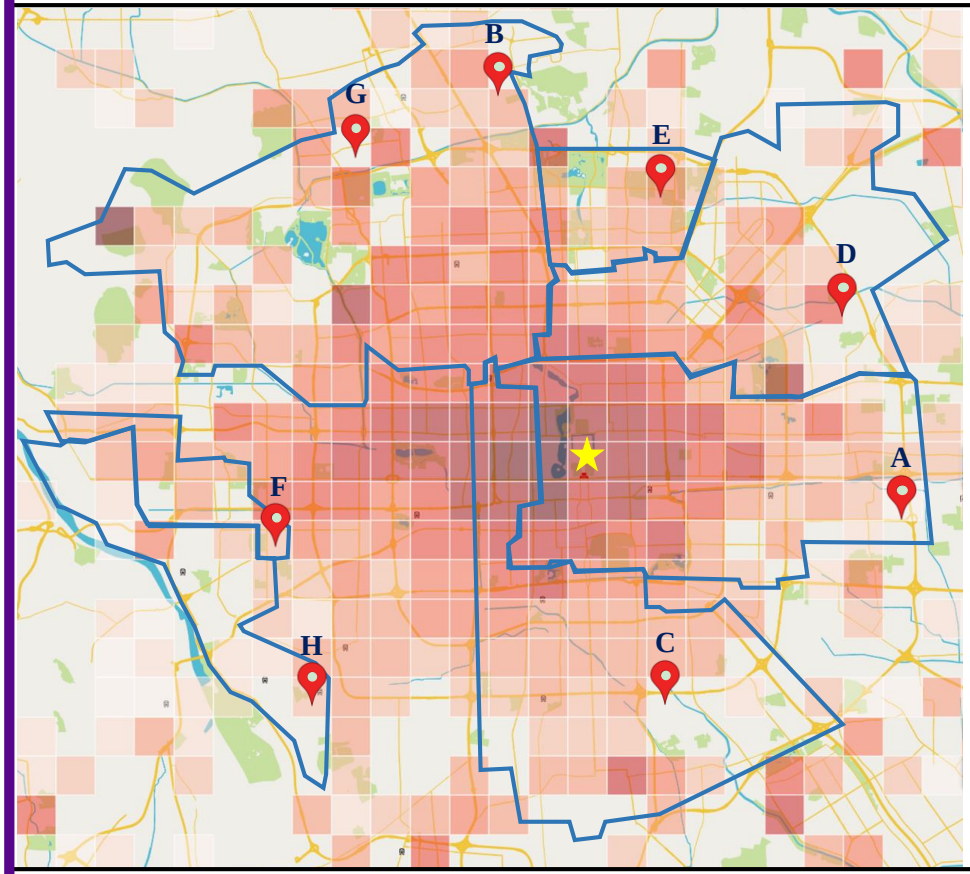


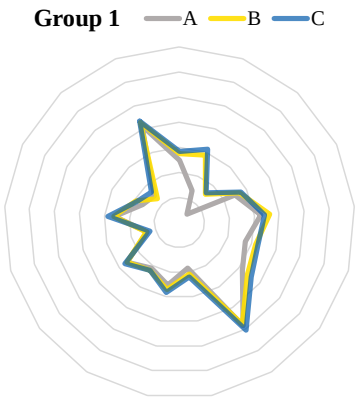
1. High ERY & ROX levels downstream of WWTP
2. High concentrations of AZI & TYL downstream of AFOs & WWTPs
3. AZI negatively correlated to sucralose (difference sources?)

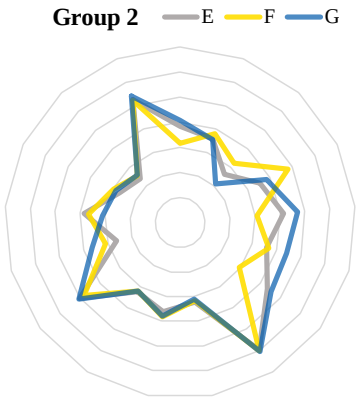
Wastewater-based epidemiology can further inform CEC loads into Chesapeake Bay river systems

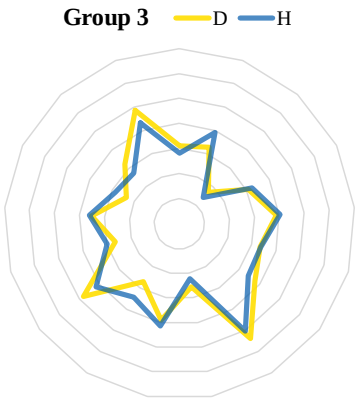
Beijing sewersheds (WWTP A-H) and housing price (heat map; darker = more expensive)

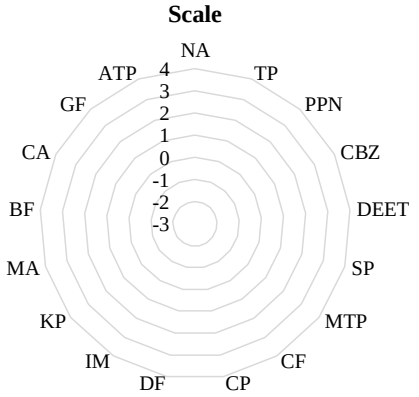
Population-normalized mass load of CECs (g d^{-1} (10^4 people)$^{-1}$)







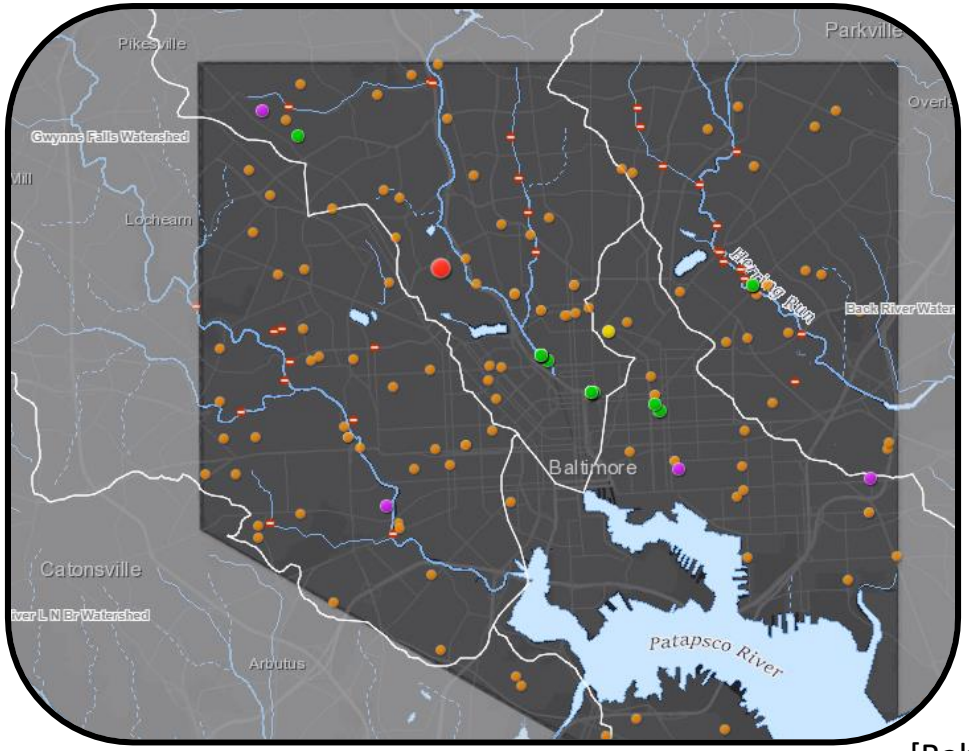




[Zhang *et al.*, 2019, *Environ. Inter.*]

Wastewater leaks and overflows are common in urban areas and may serve as an important source of CECs

"Sewage discharge into the Gwynns Falls is a major concern…Many sections of the stream…are posted due to contaminated streamflow... Continuous sewer leaks are common occurrences in Baltimore City" – 2004 water quality management plan for Gwynns Falls watershed



Spill Sends Thousands Of Gallons Of Sewage Into Marley Creek

Residents near Marley Creek in Anne Arundel County are being warned to stay away from the creek after a large sewage spill sends tens of thousands of gallons of sewage into the water.

Sewage Spill Prompts Deep Creek Lake Restrictions

Garrett County officials say about 36,000 gallons of sewage spilled into a creek that flows into Deep Creek Lake.

Md. Bans Swimming, Fishing, Kayaking In Patapsco River Due To Sewage Spill

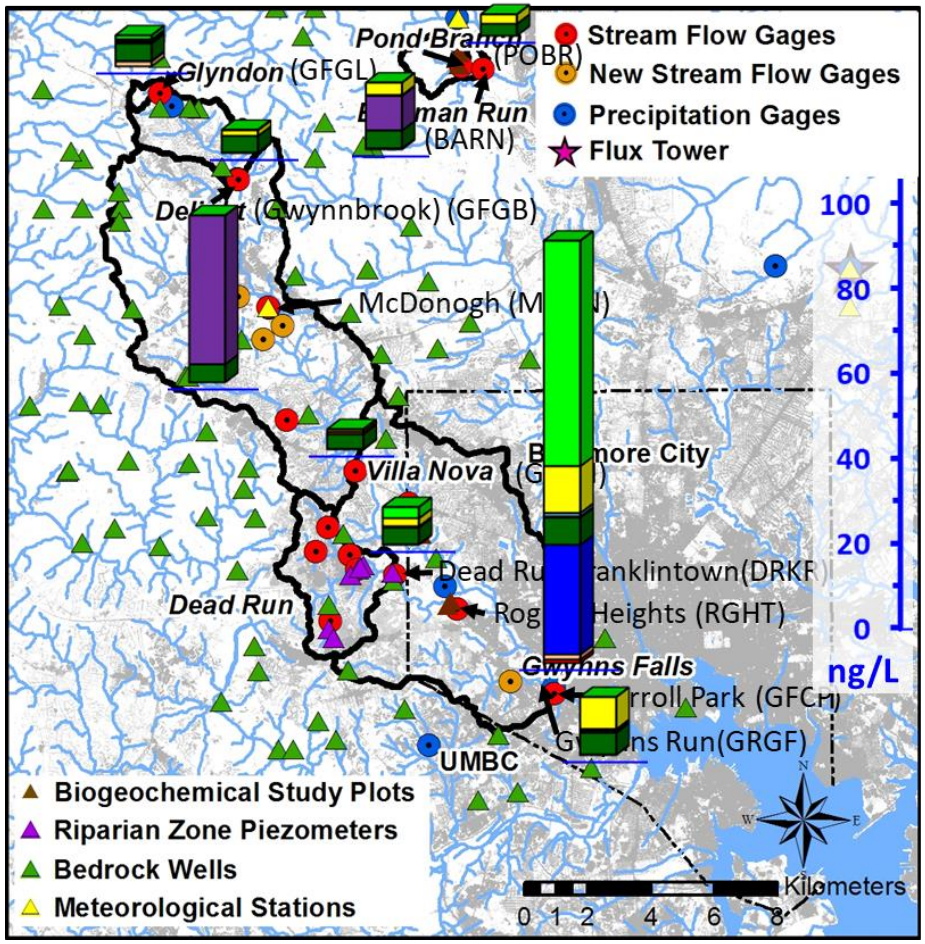
Tens of millions of gallons. That's how much raw sewage has flowed into the Patapsco River this week.

Frederick Says Water Restored After Sewage Spill

Frederick City officials say water quality has improved in Carroll Creek and the Monocacy River after 3.5 million gallons of raw sewage spilled from a waste water treatment plant last week.

[Baltimore DPW]

Antibiotic levels in the Gwynns Falls watershed suggested leaking urban wastewater infrastructure



Compound	Detection frequency (%)	Maximum concentration (ng/L)
Ciprofloxacin	1.6	49
Ofloxacin	2.9	200
Azithromycin	4.5	13
Clarithromycin	5.7	280
Erythromycin	**40.2**	**54**
Roxithromycin	2.5	327
Tylosin	2.5	4.9
Sulfadimethoxine	3.3	7.1
Sulfadimidine	4.1	6.7
Sulfamethoxazole	**37.3**	**71**
Doxycycline	9.4	365
Methacycline	2.5	215

Ofloxacin **Azithromycin** **Clarithromycin** **Erythromycin** **Roxithromycin**

Tylosin **Sulfadimethoxine** **Sulfadimidine** **Sulfamethoxazole** **Doxycycline**

Estrogens & UV-filters were also present and accumulated in crayfish, highlighting toxicity concerns

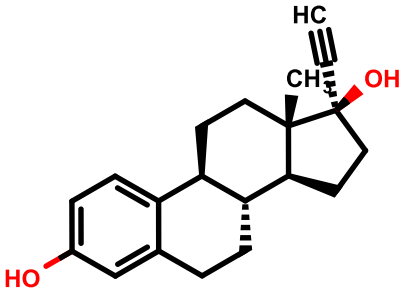
[He *et al.*, 2017, *J. Chromatogr. A*]

Table 2
Concentrations (ng/g lyophilized tissue) of analytes in the tissue of aquatic organisms. Error is standard deviation (n = 3).

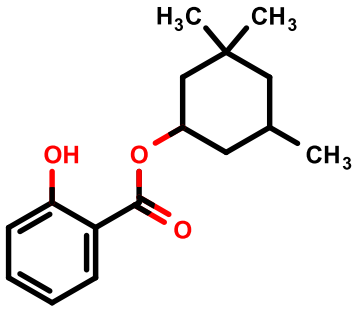
Organism	Site[a]	EE2	E2	E1	BP-3	4-MBC	OC	EHMC	HMS
Eastern crayfish	BARN	n.d.[b]	n.d.	n.d.	n.d.	214 ± 23	60.6 ± 9.0	63.5 ± 7.2	399 ± 48
	DR1	n.d.	n.d.	n.d.	37.9 ± 4.4	352 ± 12	5.0 ± 0.1	n.d.	113 ± 7
	DR2	n.d.	n.d.	n.d.	n.d.	75.3 ± 11	37.1 ± 3.9	83.0 ± 5.1	263 ± 43
	DR3	n.d.	n.d.	n.d.	51.4 ± 2.2	97.8 ± 11	6.7 ± 0.3	n.d.	108 ± 3
	DR4	n.d.	n.d.	n.d.	n.d.	106 ± 17	113 ± 6	n.d.	260 ± 16
	DR5	17.1 ± 1.6	n.d.	n.d.	23.7 ± 0.3	112 ± 12	4.5 ± 0.4	n.d.	201 ± 20
	DRKR	n.d.	n.d.	n.d.	29.5 ± 0.3	190 ± 18	3.4 ± 0.2	n.d.	77.6 ± 7.5
Red swamp crayfish	ARO	15.5 ± 0.8	n.d.	n.d.	42.8 ± 5.1	n.d.	2.6 ± 0.3	n.d.	174 ± 7
Eastern oyster	ARO	n.d.	n.d.	n.d.	51.7 ± 2.5	n.d.	21.5 ± 3.8	n.d.	211 ± 21
	CBCR-2	n.d.	n.d.	n.d.	40.6 ± 7.5	n.d.	n.d.	241 ± 35	143 ± 40
	CBCR-3	19.1 ± 1.2	n.d.	n.d.	36.8 ± 2.5	n.d.	6.6 ± 0.7	155 ± 20	56.1 ± 5.6
Hooked mussel	CBCR-3	15.3 ± 0.7	15.5 ± 0.5	70.3 ± 3.2	35.4 ± 1.5	n.d.	14.4 ± 0.6	240 ± 13	107 ± 4

[a] BARN, Baisman Run; DR1-5, Dead Run Sites 1–5; DRKR, Dead Run at Franklintown; ARO, Aquatic Research Organisms; CBCR sites were located at the mouth of the Chester River, Chesapeake Bay.
[b] n.d. = not detected.

EE2: 17.1 ± 1.6 ng/g

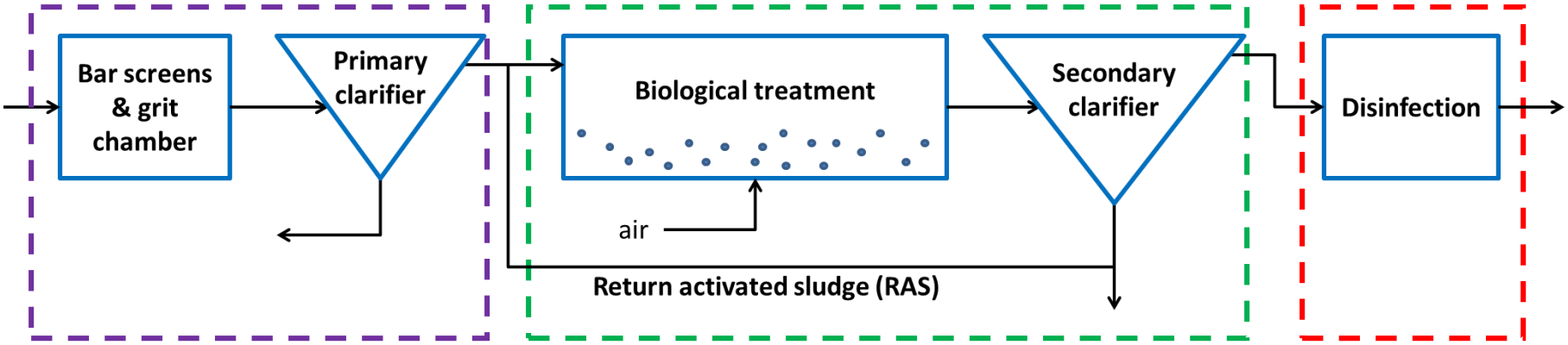


HMS: 399 ± 48 ng/g



CEC removal in WWTPs

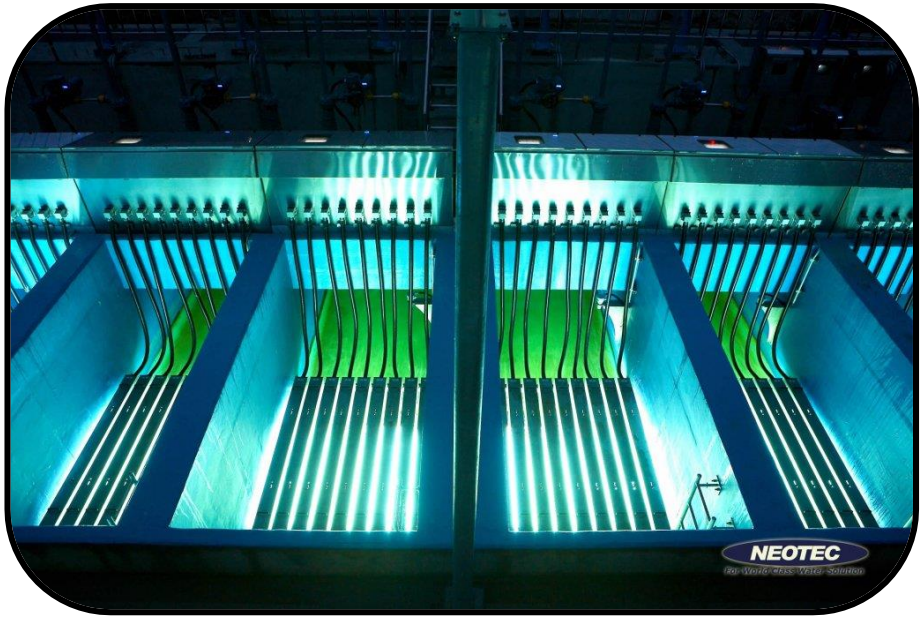
WWTPs offer opportunities to sorb and transform CECs through various unit processes



Process	CEC removal
Bar screens, grit chamber, primary clarifier	Minimal, any removal would come from sorption processes already occurring in collection system
Biological treatment	(1) Some biological transformation (metabolism) of CECs may occur but removal efficiency varies widely; (2) some sorption/partitioning of CECs into the RAS/WAS can occur, resulting in CEC loads in biosolids
Transformation during disinfection/oxidation	Some CECs readily react with chlorine, chloramines, or UV light to undergo transformation reactions
Advanced processes	Typical options include activated carbon (sorption-based), nanofiltration or reverse osmosis membranes (physicochemical rejection), or advanced oxidation (generation of $^{\bullet}OH$, *e.g.*, UV-H_2O_2)

UV disinfection is becoming more prevalent due to safety, cost, and operational advantages

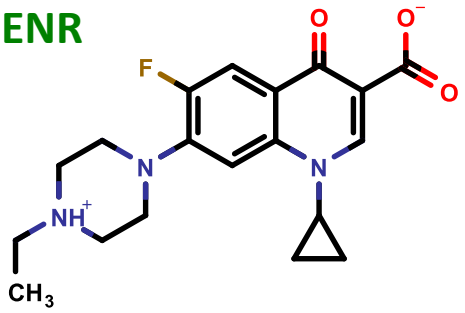
Over **46% of wastewater treatment plants** in North America are now using UV disinfection [Trojan, 2012].



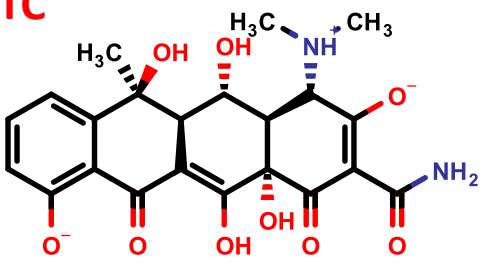
The **Catskill–Delaware Ultraviolet Water Treatment Facility** in New York City has a 2240 MGD capacity and almost 12,000 lamps.

Dissolved chemicals, like antibiotics, absorb the energy from UV light and undergo chemical transformations

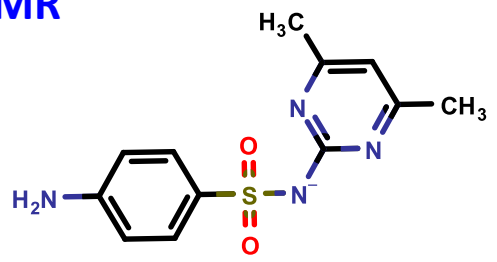
ENR

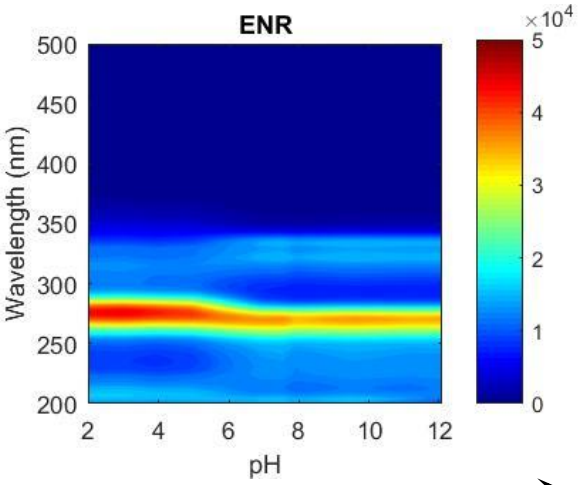


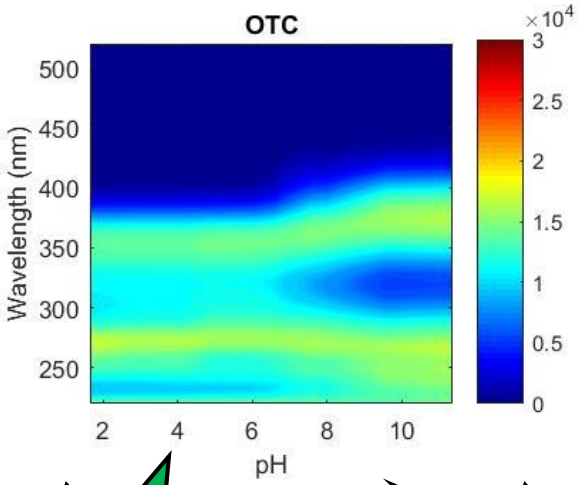
OTC

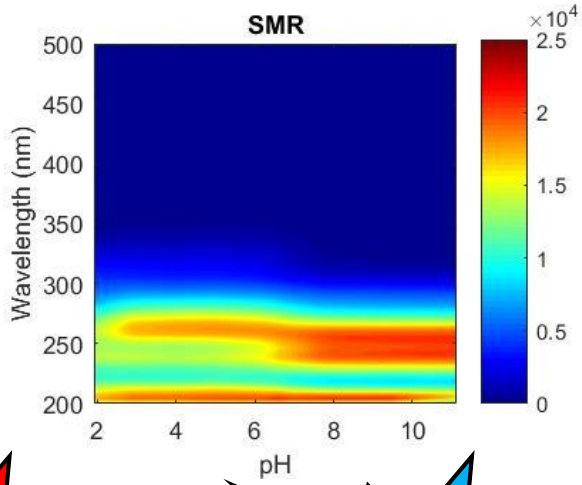


SMR









Fluence needed for 90% transformation:

500 mJ/cm²

12,000 mJ/cm²

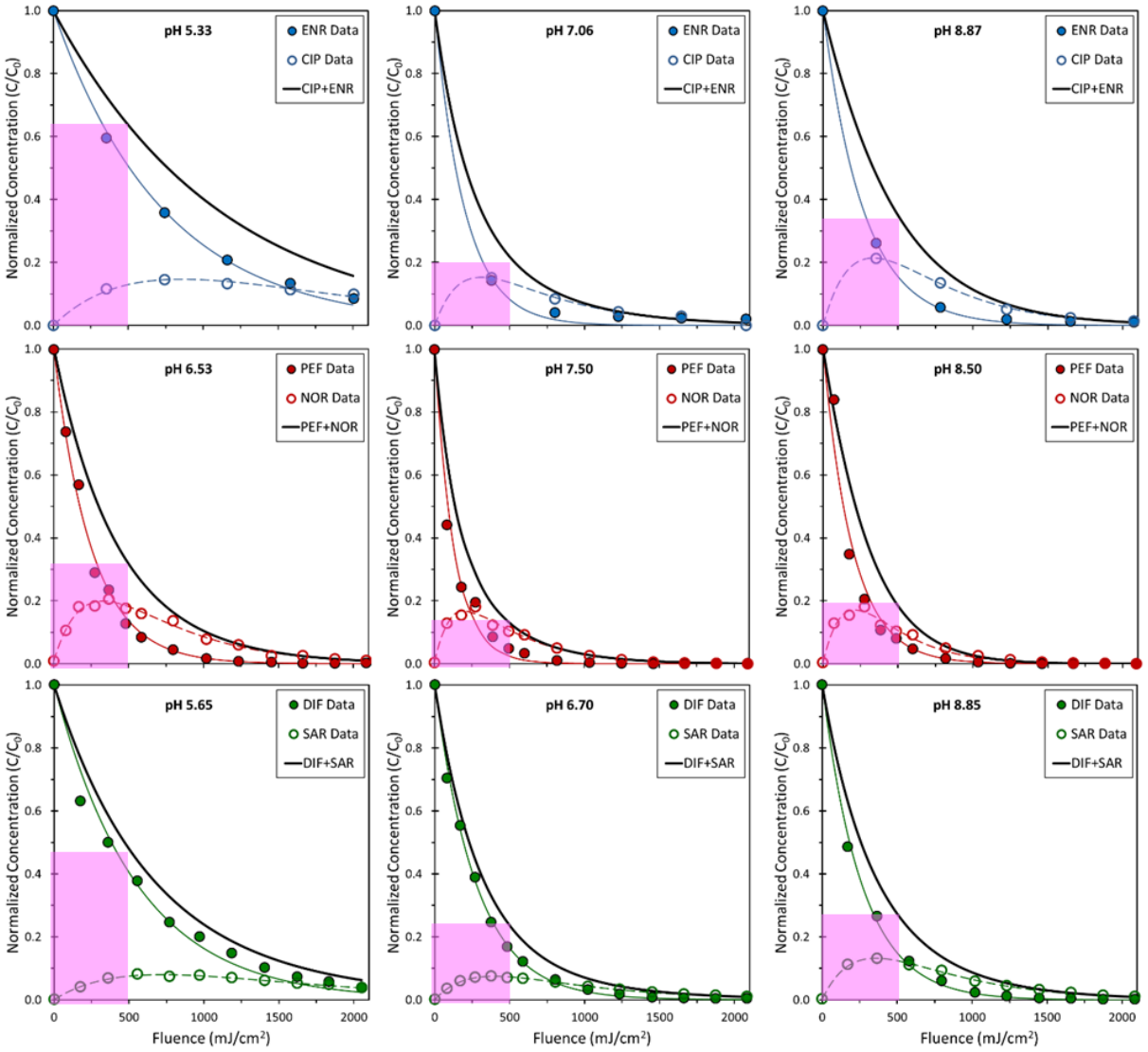
3,000 mJ/cm²

Direct photolysis results in some transformation (good news), but the products are also antibiotics (bad news)

ENR → CIP

PEF → NOR

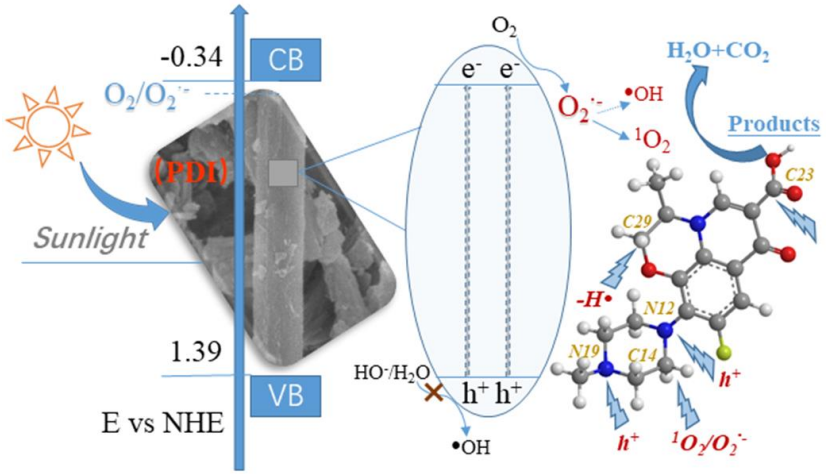
DIF → SAR



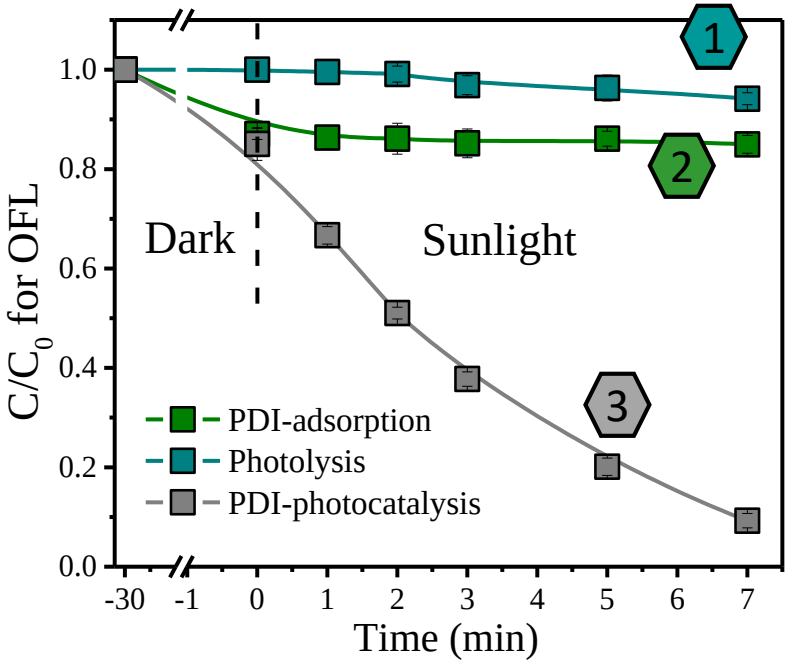
[Snowberger *et al.*, 2016, *ES&T*]

Sustainable advanced oxidation processes are one option to improve treatment efficiency

My collaborators (Tsinghua University) and I recently reported a **sunlight-activated photocatalyst** that provides fast transformation of fluoroquinolone antibiotics.



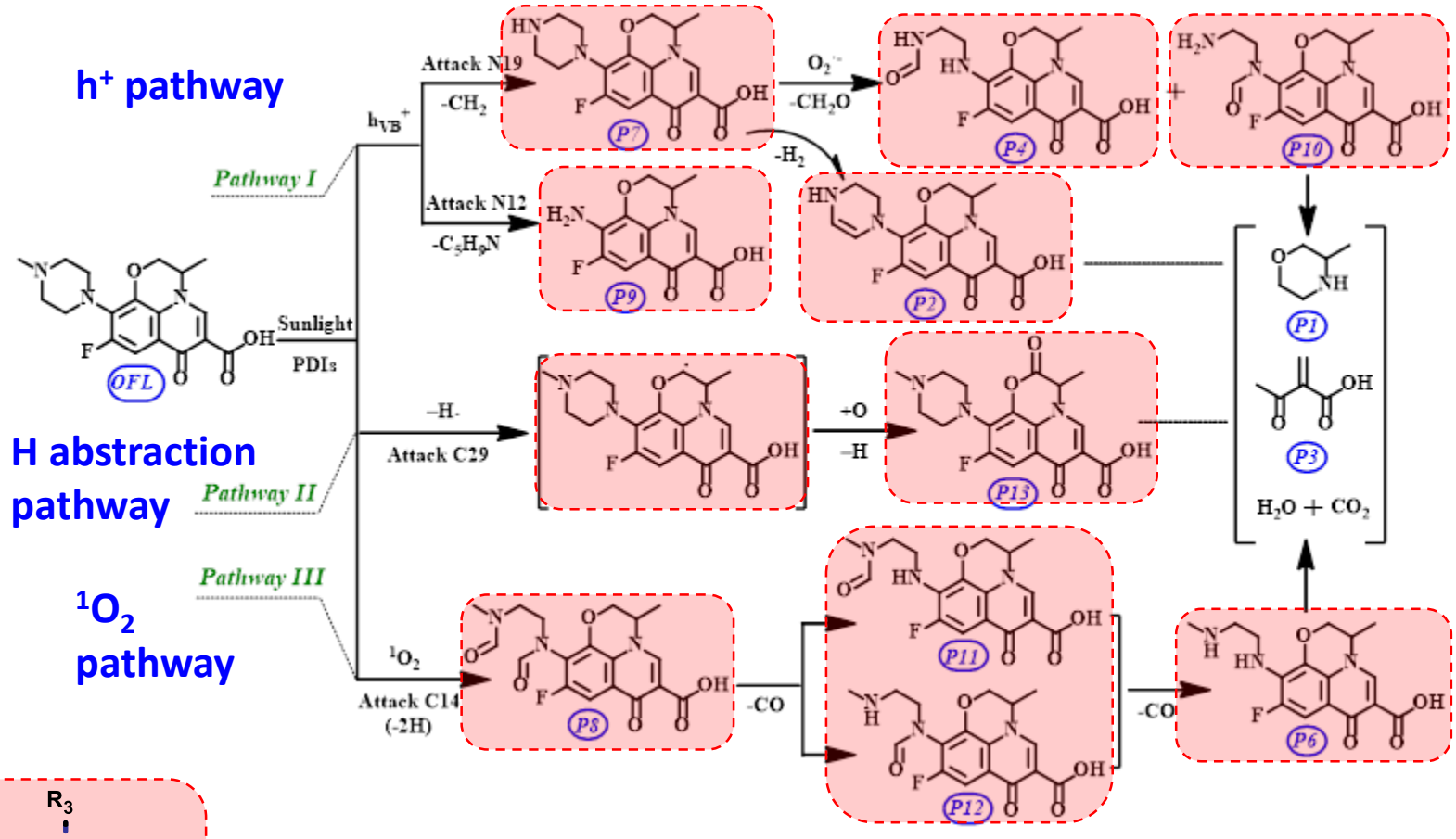
[Chen*, Blaney* *et al.*, 2019, *ES&T*]

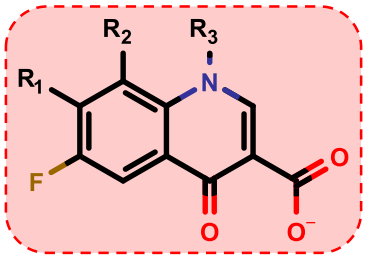


1. Negligible sunlight photolysis
2. Up to ~15% sorption (~ 6 mg g^{-1})
3. Fast sunlight photocatalysis

Conditions: C_0 = 8 mg L^{-1}; PDI = 200 mg L^{-1}; pH 5.6; natural light (Beijing), 45-55 mW cm^{-2}

Reaction pathways were identified & most transformation products are expected to retain antimicrobial activity





fluoroquinolone pharmacophore

Attack mechanisms were considered using kinetics, frontier electron density calculations, & transformation products were identified by UPLC-Q-TOF-MS

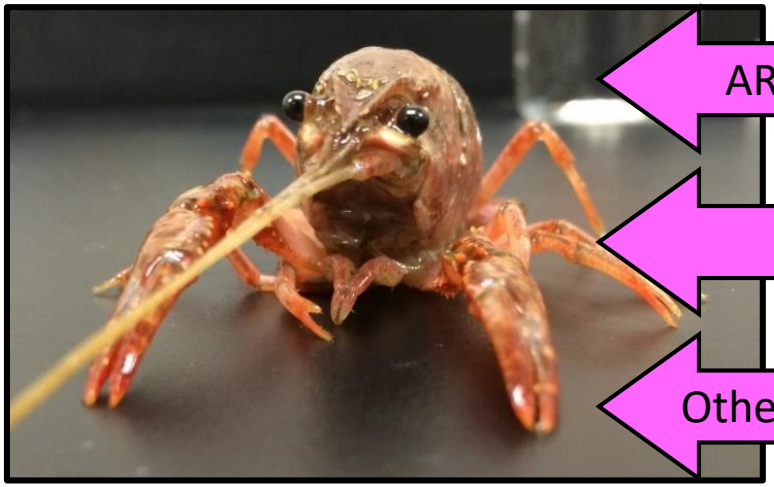
Conclusions

Concluding remarks

WWTPs

AFOs

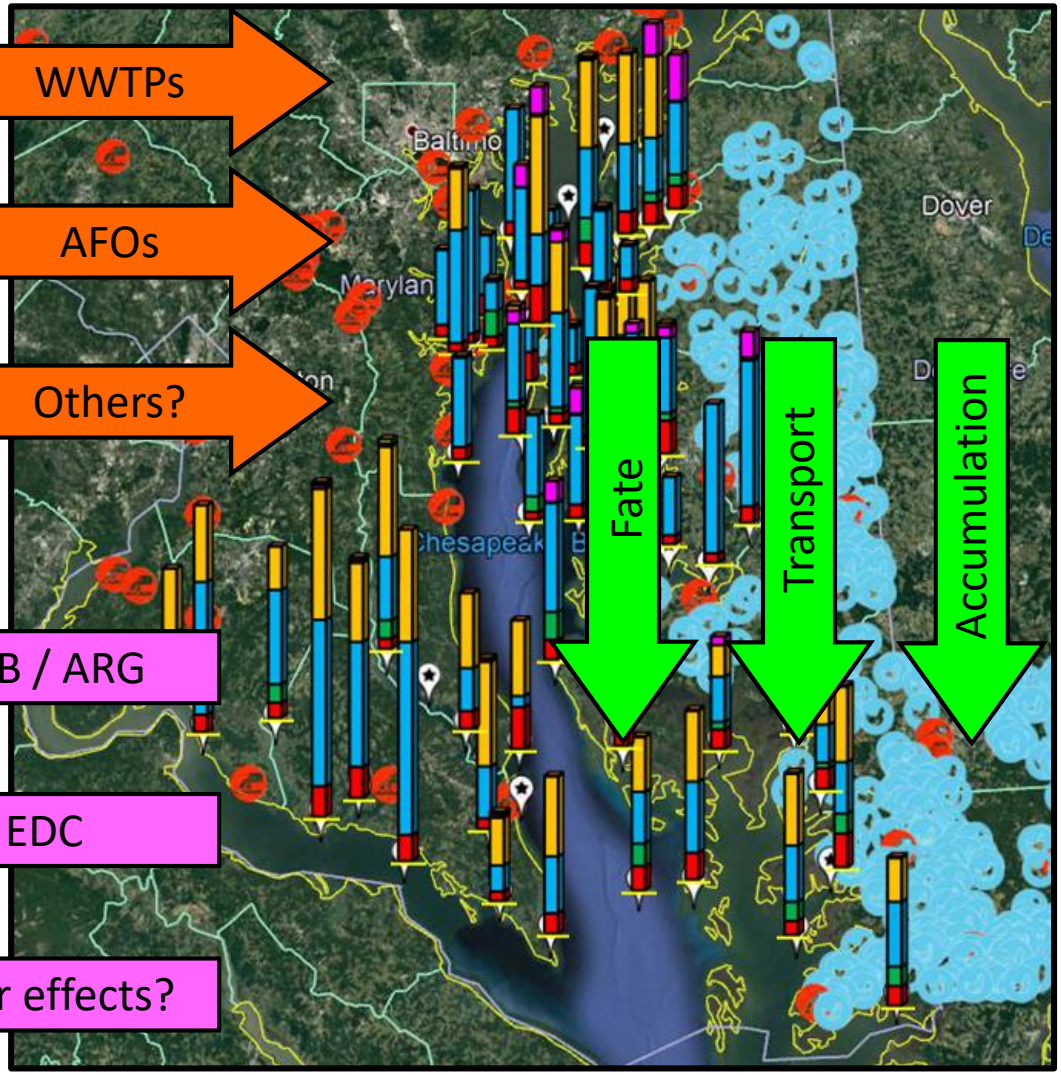
Others?



ARB / ARG

EDC

Other effects?



My great team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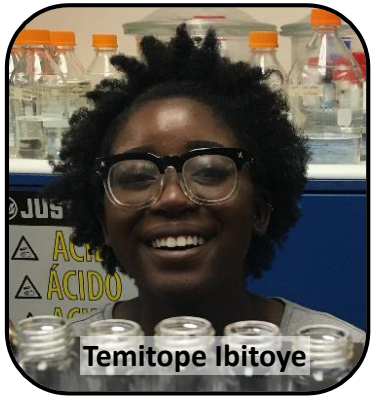
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US Army Corps of Engineers
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Thanks for your attention

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