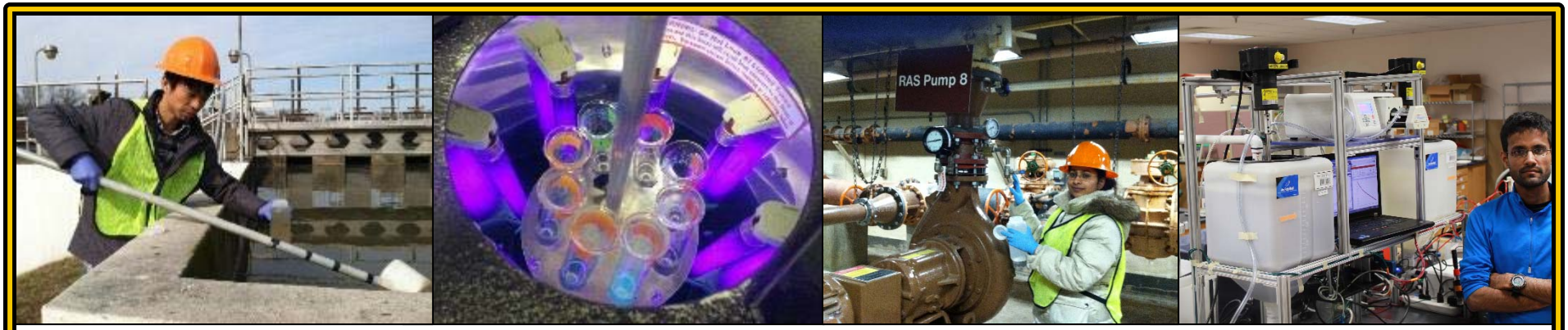


Contaminants of Emerging Concern in Urban Settings

Lee Blaney

Department of Chemical, Biochemical, and Environmental Engineering

University of Maryland Baltimore County (UMBC)

Chesapeake Bay Program

Toxic Contaminants Workgroup

March 14, 2018

Chesapeake Bay Program

Science. Restoration. Partnership.

UNIVERSITY OF MARYLAND BALTIMORE COUNTY

UMBC

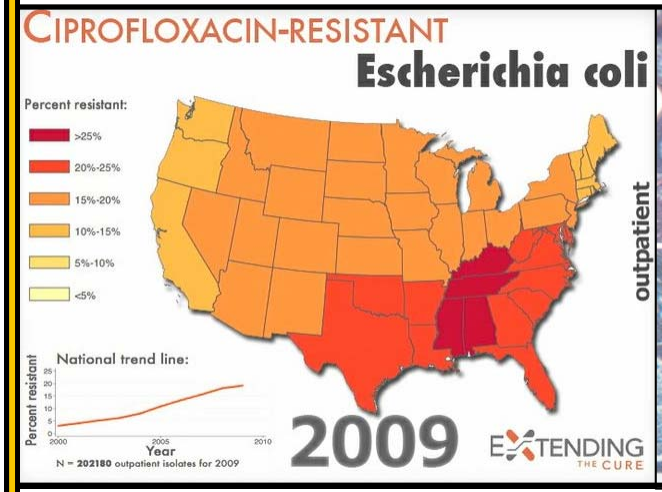
1966

Priority* CECs affect ecological and human health

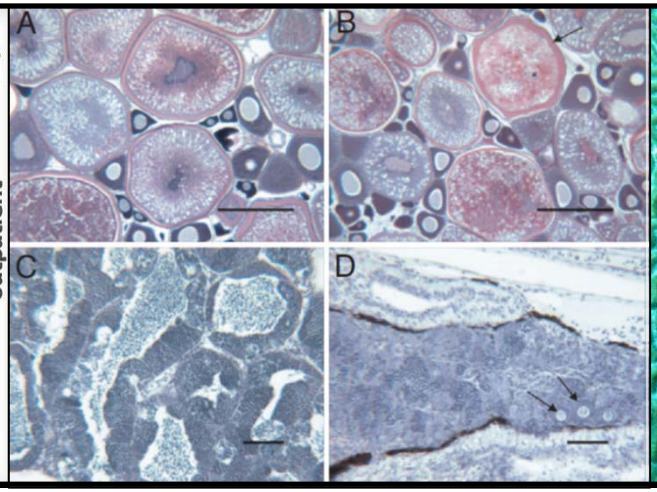
Antibiotics exert a selective pressure for resistant organisms at environmentally-relevant concentrations

Estrogenic hormones affect endocrine systems at concentrations as low as 1-10 ng/L, and these effects can cause population crashes

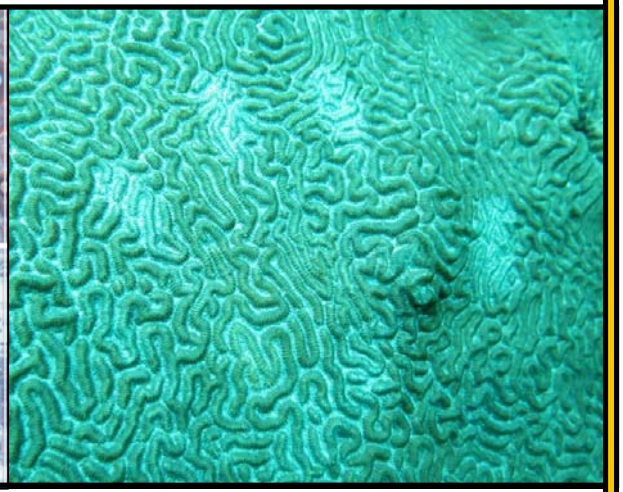
UV-filters exhibit estrogenic activity, and were recently shown to be toxic to corals at < 100 ng/L



http://wellcommons.com/weblogs/health-beat/2011/apr/11/antibiotic-resistance-mapped-across-the-/



Kidd *et al.*, 2007



https://newsdeeply.imgix.net/20170615093325/Sunscreen-hand-print-on-coral.jpg

My goals for today

1. To discuss our ongoing work on the detection of contaminants of emerging concern (CECs) in **Chesapeake Bay water, sediment, and oysters**; and,

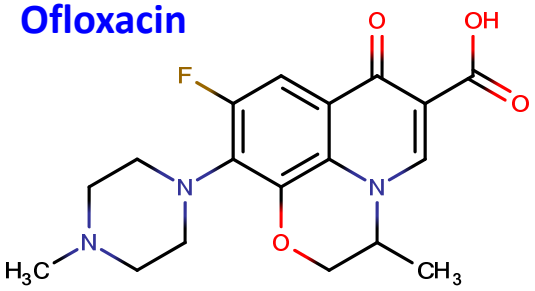
2. To describe the occurrence of CECs in an **urban watershed** that is not impacted by expected sources (*e.g.*, wastewater effluent, animal feeding operations)

Analytical Methods

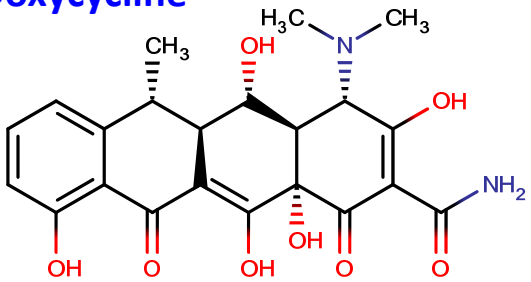
We measure a large suite of CECs…

…including fluoroquinolones, sulfonamides, tetracyclines, macrolides, estrogenic and androgenic hormones, and UV-filters (sunscreens).

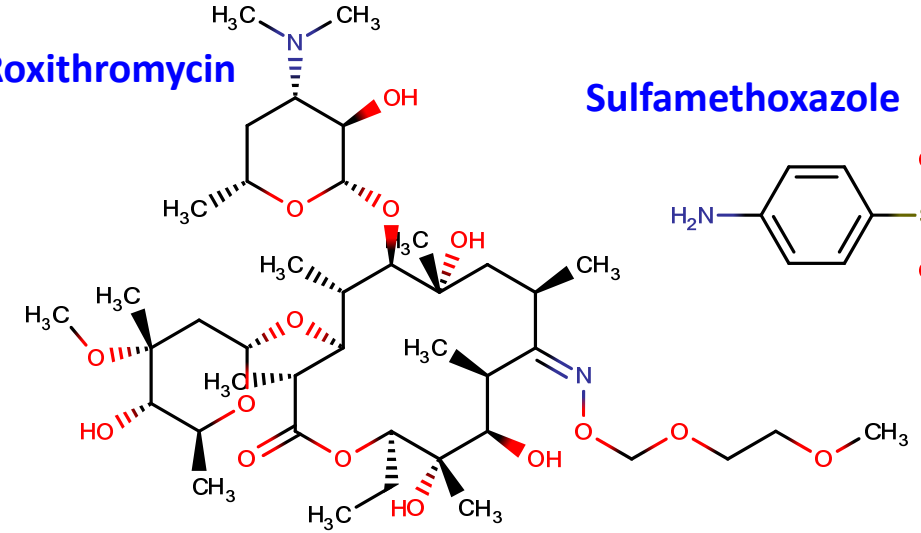
Ofloxacin



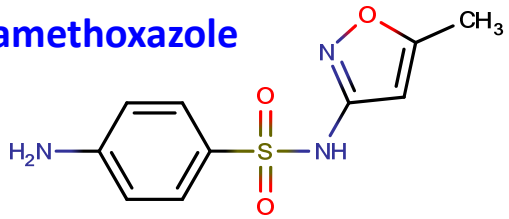
Doxycycline



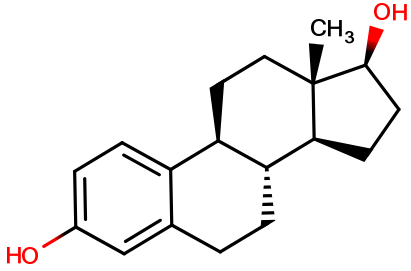
Roxithromycin



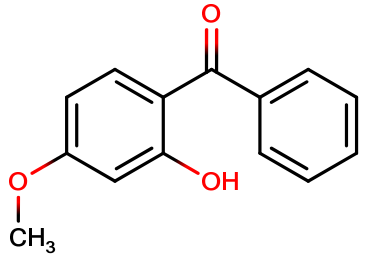
Sulfamethoxazole



17β-estradiol



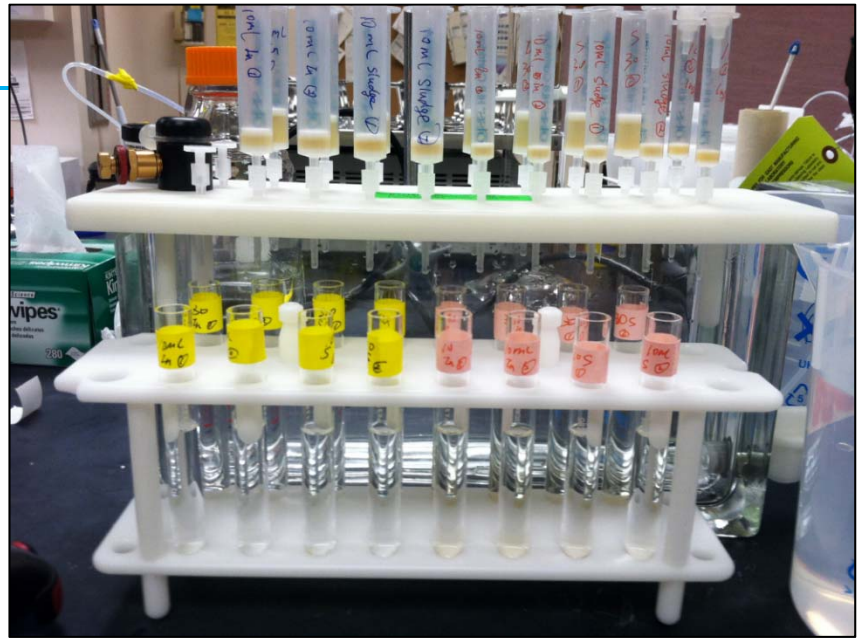
Oxybenzone

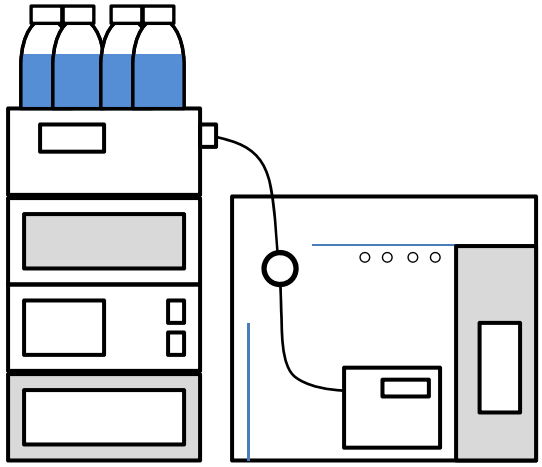


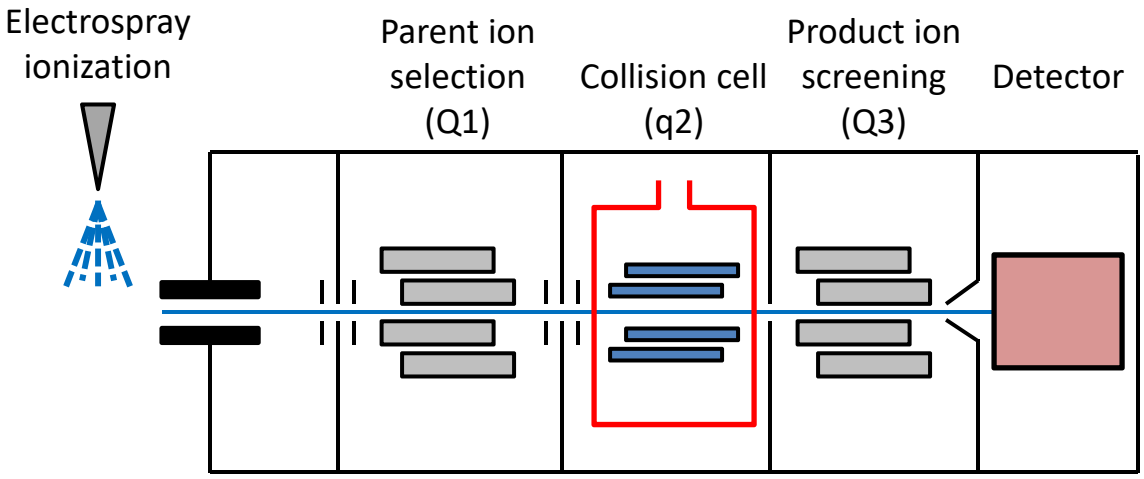
SPE with LC-ESI-MS/MS

Solid-phase extraction (SPE) is used to remove interferences and concentrate analytes

Liquid chromatography with tandem mass spectrometry (LC-MS/MS) is used to selectively and sensitively measure multiple analytes



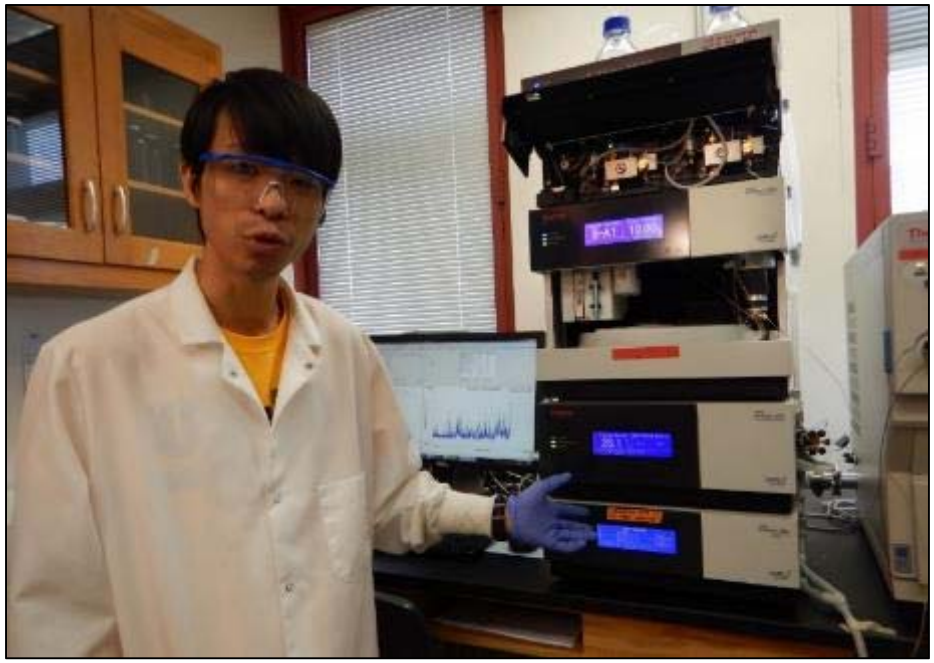


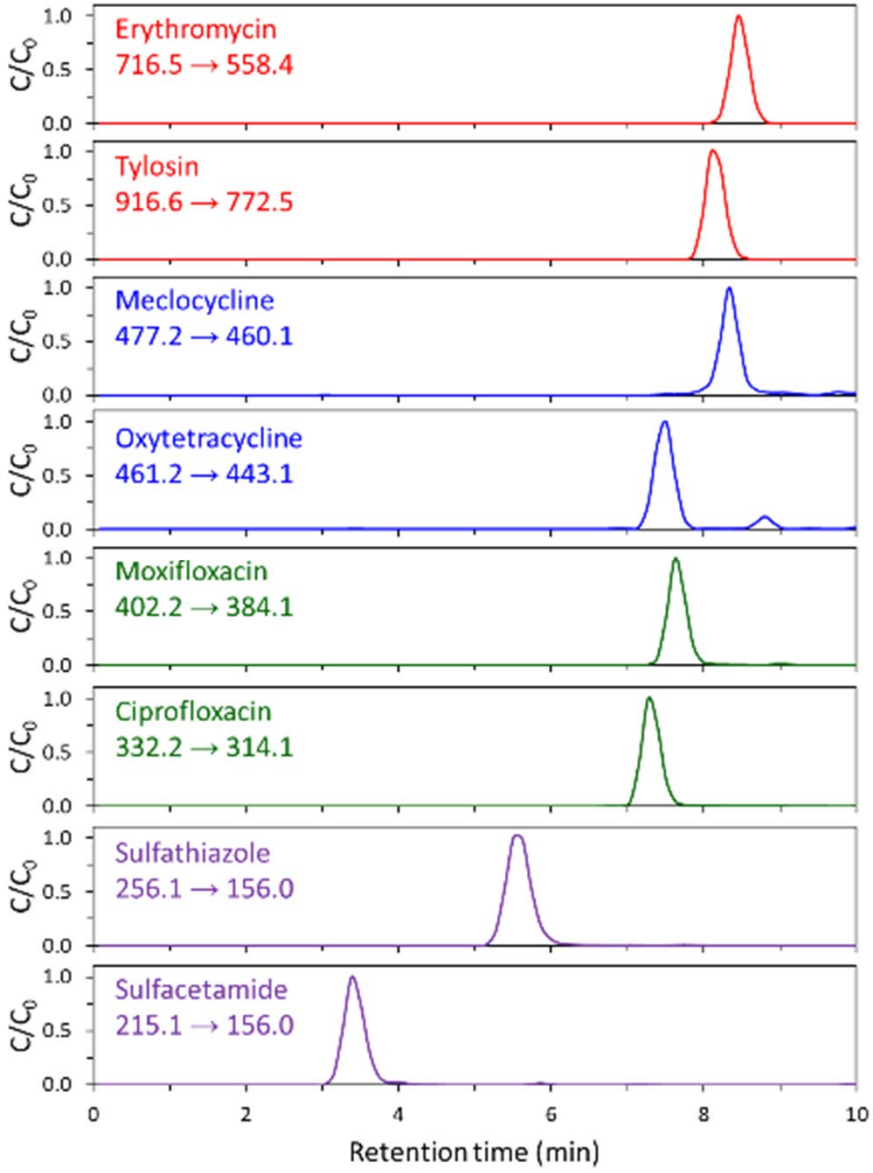


Now measuring >70 CECs in environmental samples

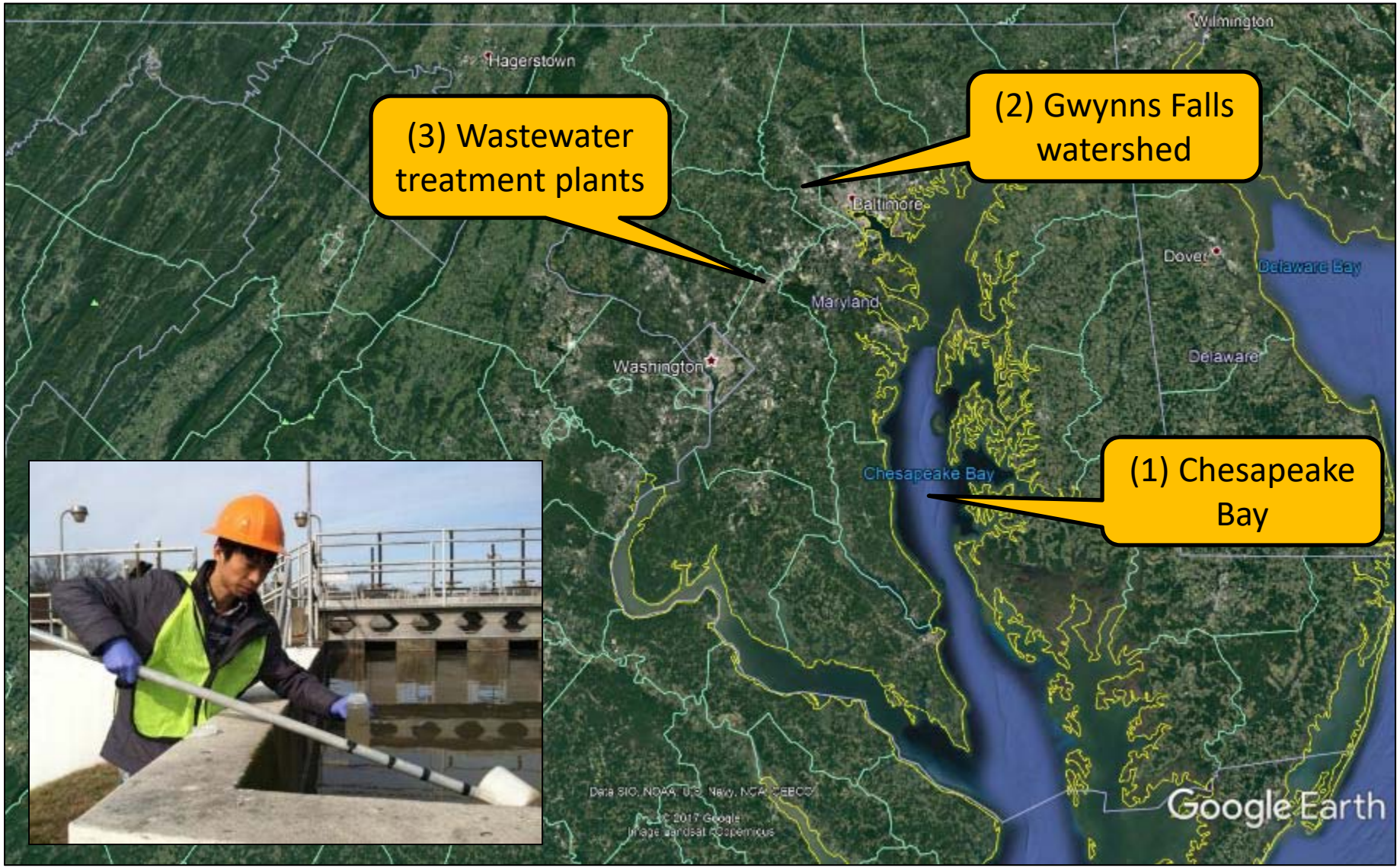
For the sake of brevity, full analytical methodologies are not included here (estrogens/UV-filters in He *et al.*, 2017 *J. Chromatogr. A*; antibiotics, in prep).

Limits of detection ≤ 1.5 ng/L





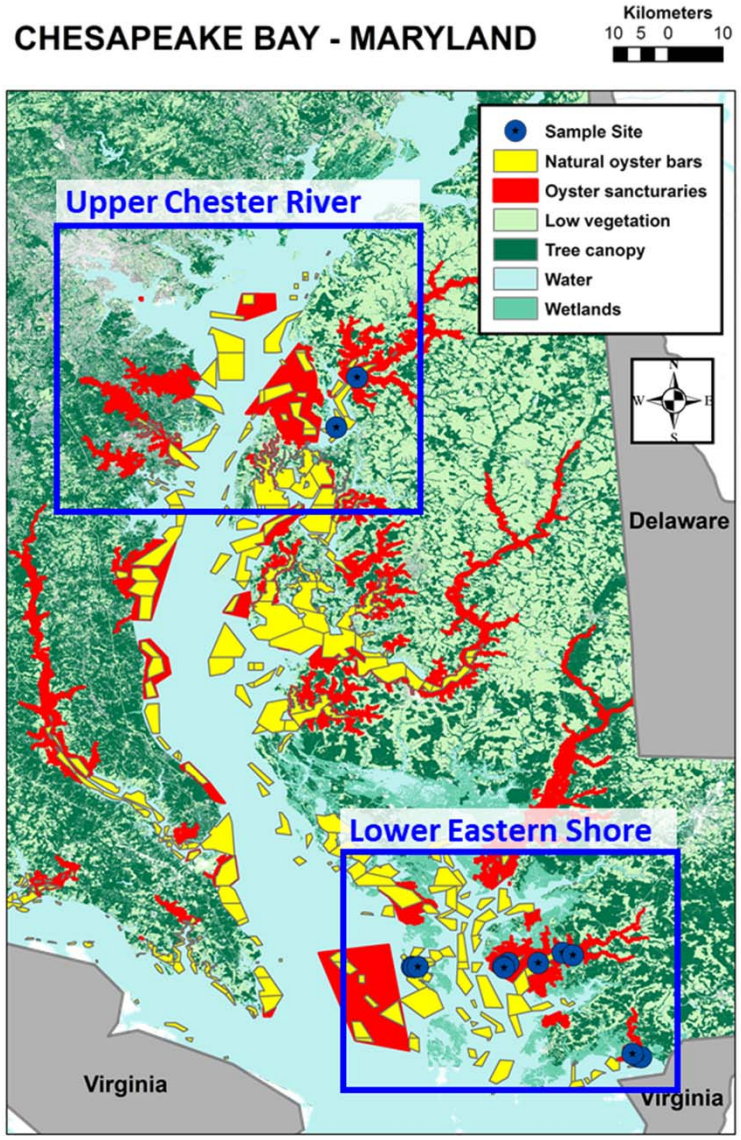
Our study of CECs in the Chesapeake Bay watershed…

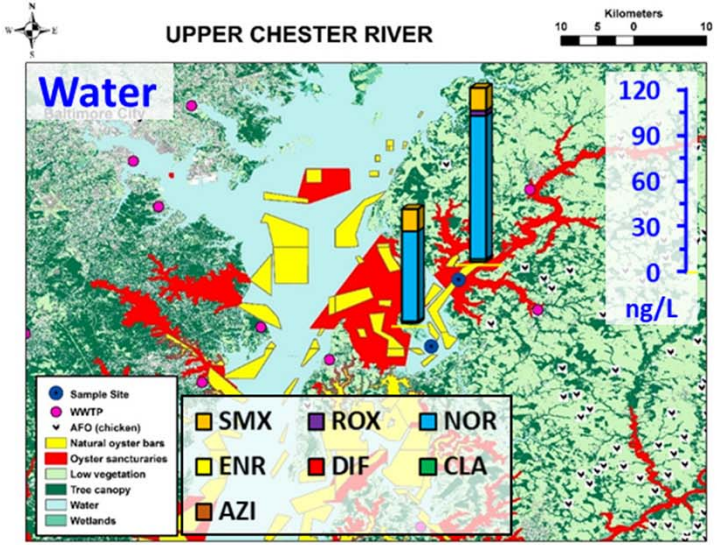


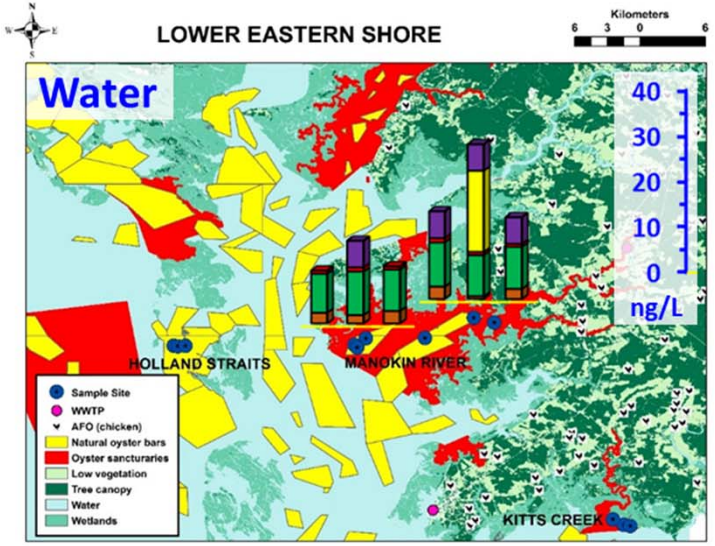
Hypothesis

CEC concentrations are low in the Chesapeake Bay due to mixing and dilution

Human- and animal-labelled antibiotics detected





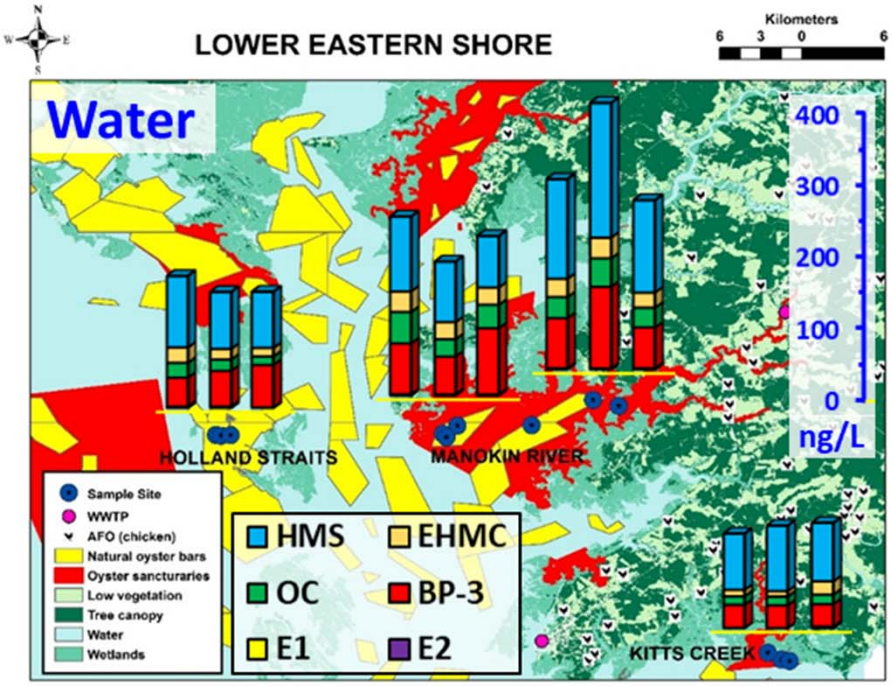


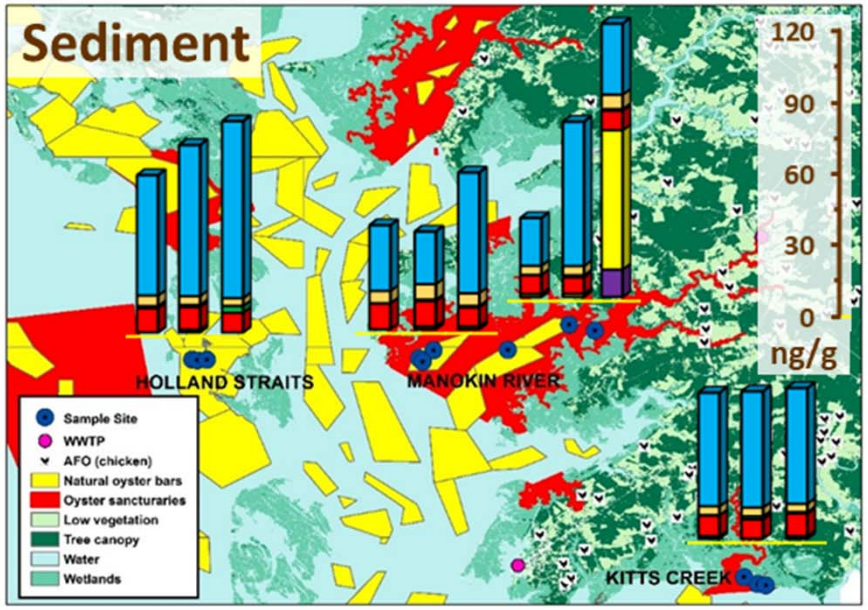
SMX	Sulfamethoxazole
ROX	Roxithromycin
NOR	Norfloxacin
ENR	Enrofloxacin
DIF	Difloxacin
CLA	Clarithromycin
AZI	Azithromycin

[He *et al.*, in prep]

UV-filters and estrogenic hormones ubiquitously present

In spring 2017, we conducted a preliminary assessment of CECs at 12 sites near Princess Anne, MD with assistance from the Maryland Department of Natural Resources (Mitch Tarnowski)



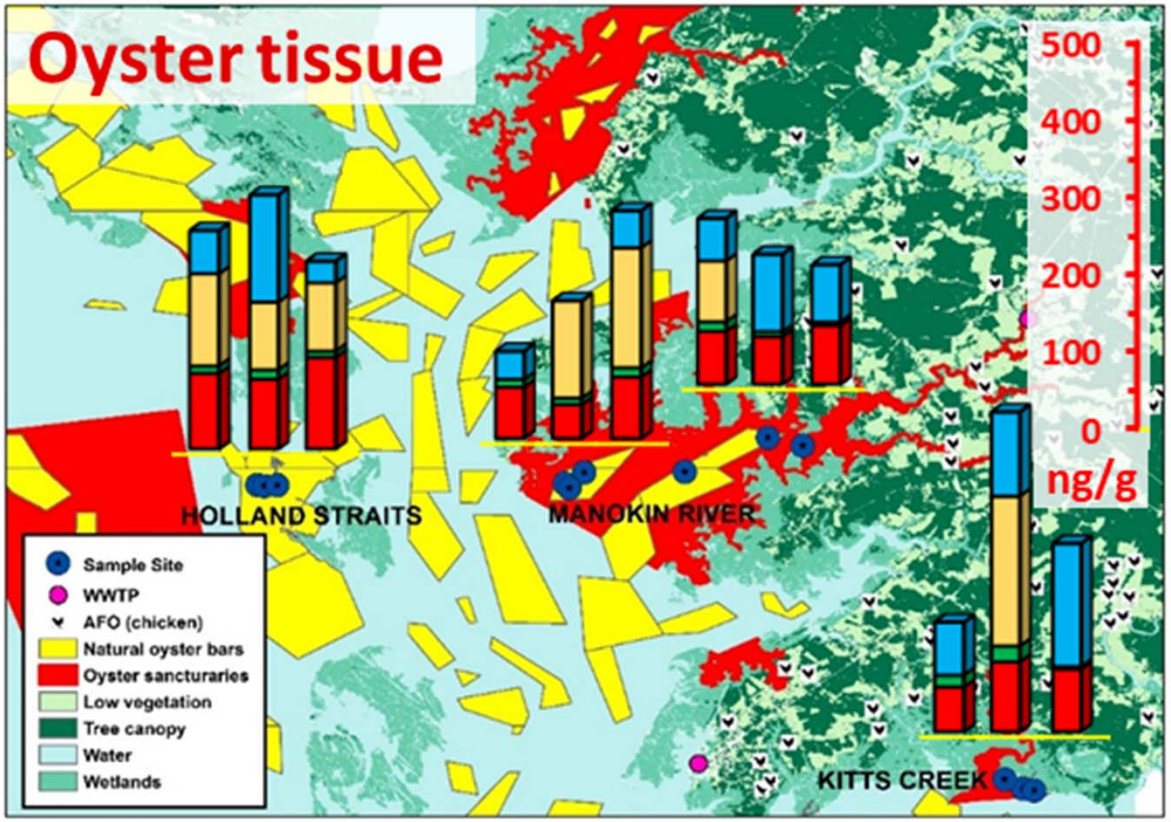


HMS	Homosalate	EHMC	Ethylhexylmethoxycinnamate
OC	Octocrylene	BP-3	Oxybenzone
E1	Estrone	E2	17β-estradiol

Base map credit: Anne Timm (USFS)

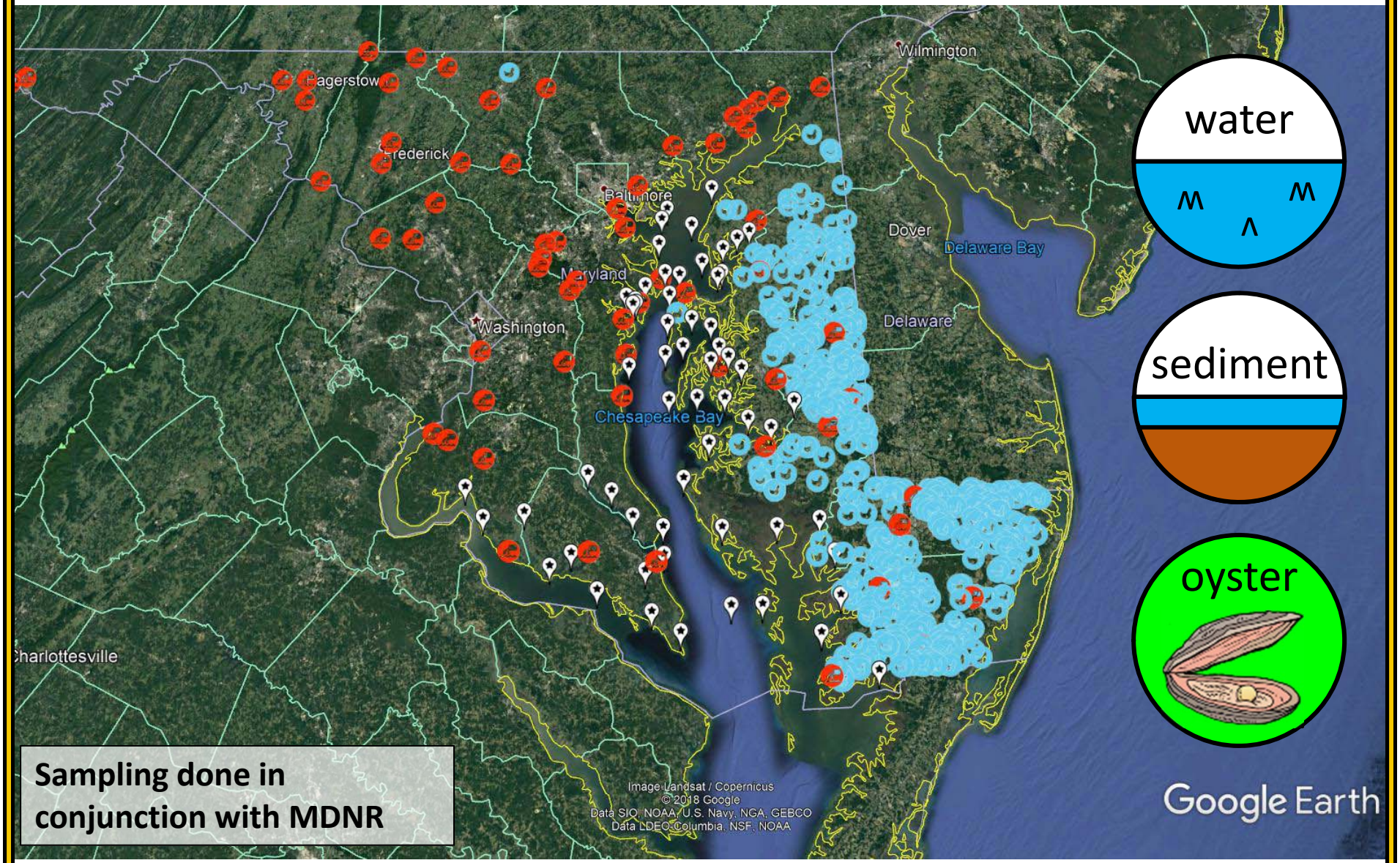
[He *et al.*, in prep]

CECs accumulate in oysters even in central channel of Bay

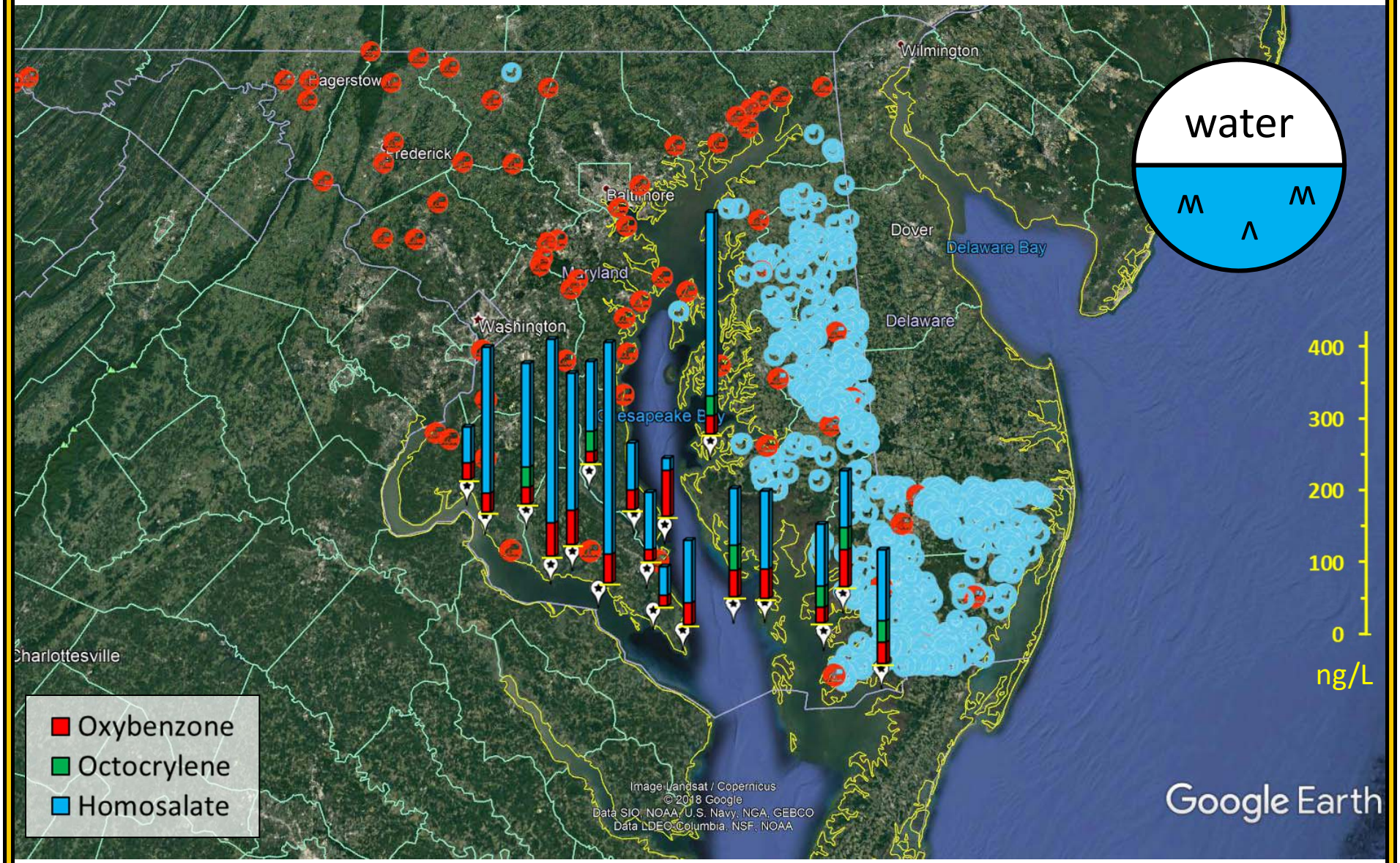


[He *et al.*, in prep]

Current sampling campaign [data being processed]



Early results suggest [CEC]s influenced by land use



"We get what we measure"

Sampling campaigns for CECs focus on expected sites

"…the selection of sampling sites primarily *focused on areas considered susceptible to contamination* from human, industrial, and agricultural wastewater."

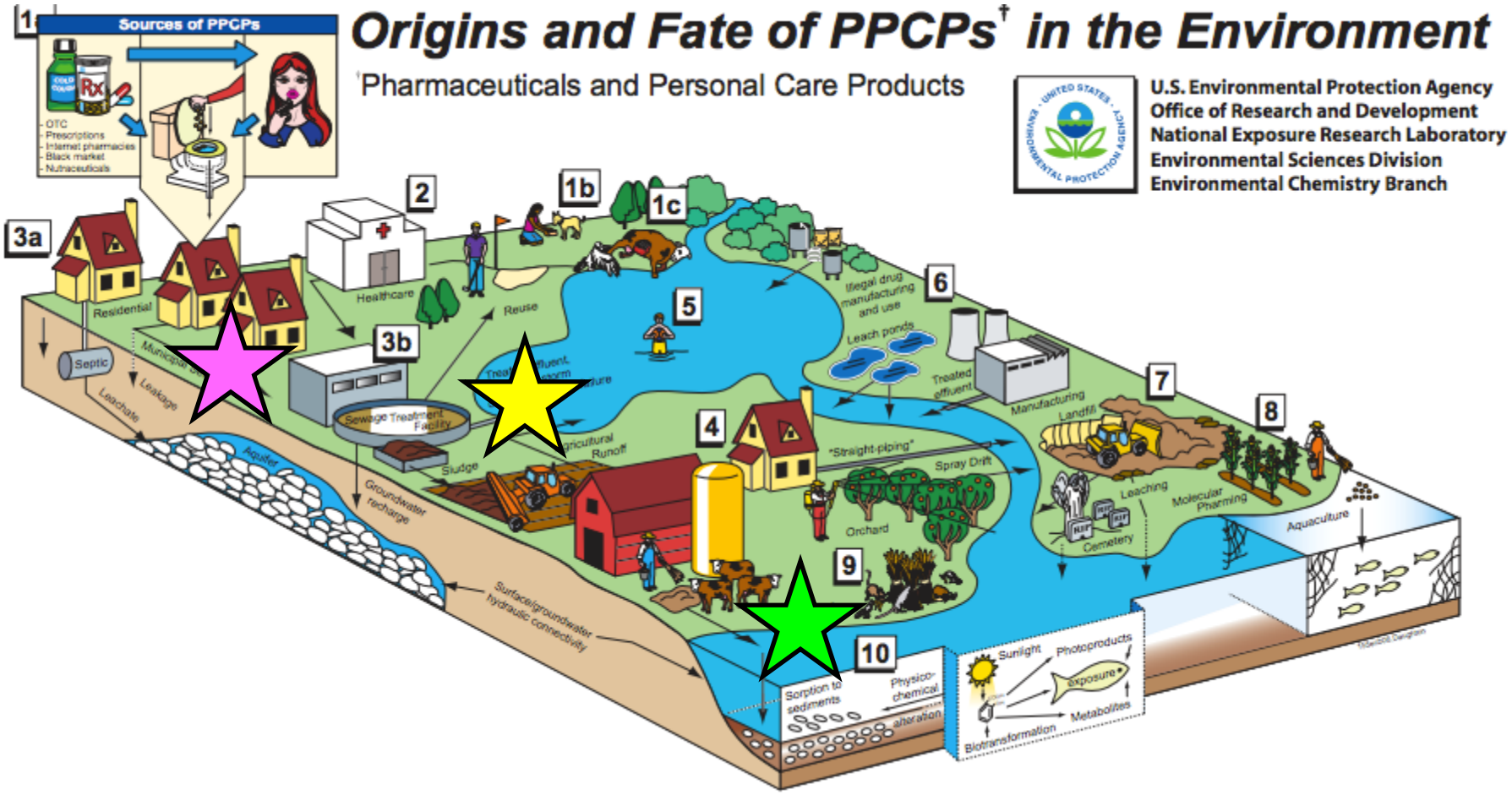
Kolpin *et al.*, 2002

"Site selection *focused on areas suspected to be susceptible to contamination* from either animal or human wastewaters (i.e. down gradient of a landfill, unsewered residential development, or animal feedlot)."

Barnes *et al.*, 2008

There have been few efforts conducted in "unimpacted" streams and watersheds.

Revisiting assumptions about CEC sources in urban environ.



Wastewater leaks are common, may be a source of CECs

Literature indicates that sewer exfiltration can be as high as 10-20% of dry weather flow; furthermore, larger leaks/spills occur on a regular basis…

"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.

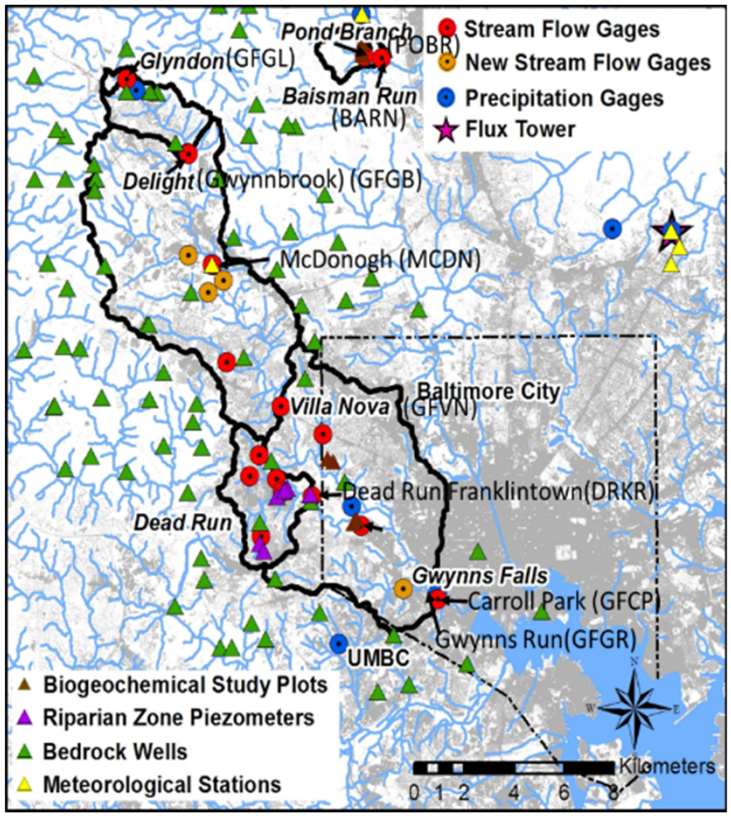
Frederick Says Water Restored After Sewage Spill

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.

Hypothesis

CECs are present in *unimpacted* urban watersheds due to leaking sewers

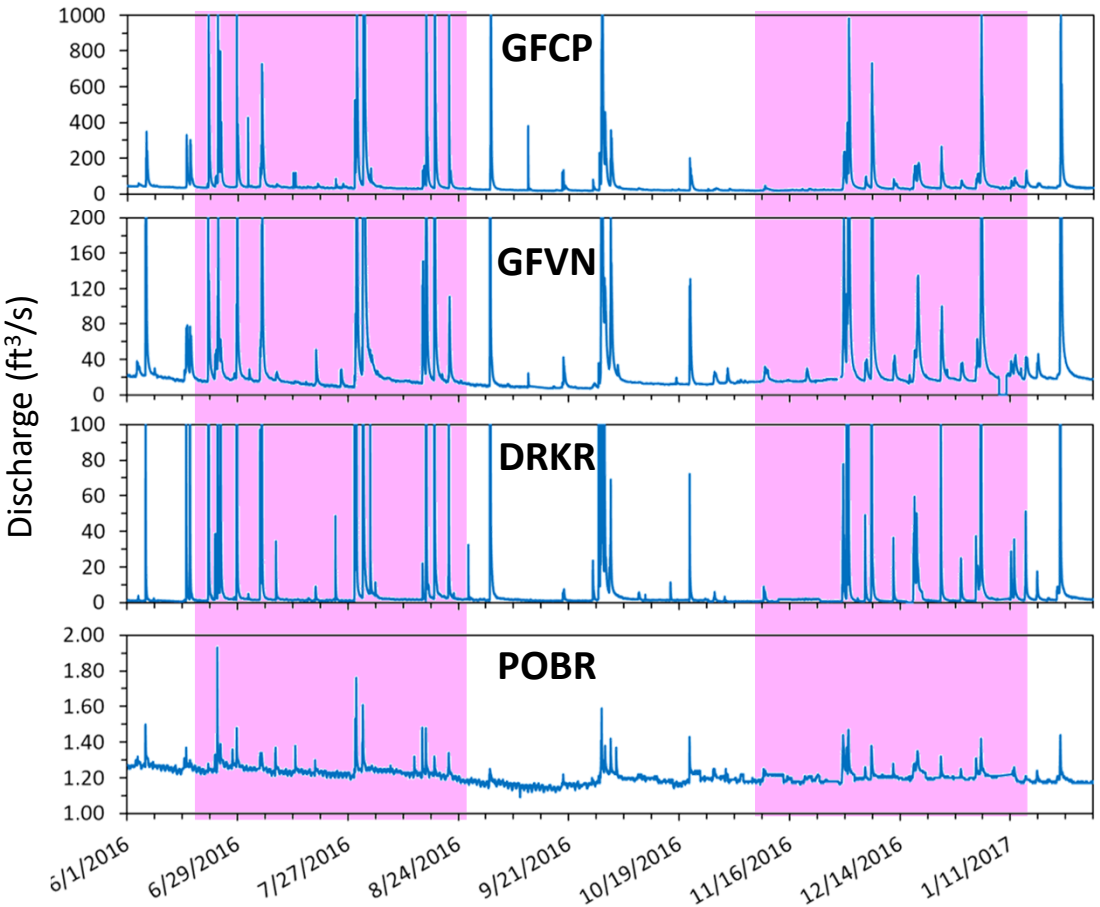
We sampled *unimpacted* urban streams



Source: Baltimore Ecosystem Study

Summer sampling
6/15/16 – 08/26/16

Winter sampling
11/8/16 – 01/12/17

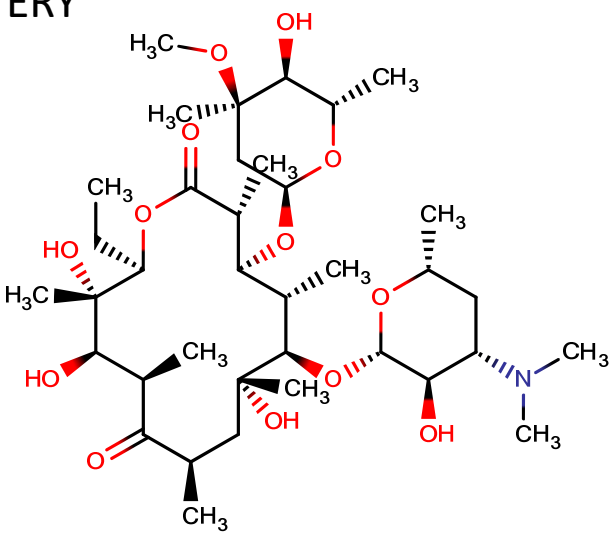


Source: USGS NWIS

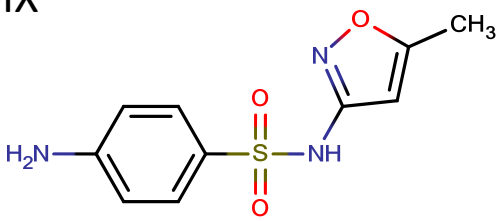
A variety of antibiotics were detected at high conc.

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

ERY



SMX



[He *et al.*, in prep]

Antibiotic detections varied by site/season

Summer – 2016

Site	Fluoroquinolone			Macrolide					Sulfonamide					Tetracycline			Other
	CIP	OFL	MOX	AZI	CLA	ERY	ROX	TYL	SCM	SDM	SDD	SMR	SMX	DC	MTC	OTC	SIL
POBR	0	0	0	0	0	1	0	0	0	0	0	0	1	0	0	0	0
BARN	0	0	0	0	1	2	2	0	0	0	1	0	6	0	1	0	0
GFGL	0	0	0	1	1	2	0	1	0	2	1	0	0	1	1	0	1
GFGB	0	0	0	0	1	2	0	0	0	0	0	0	1	2	0	0	0
MCDN	0	0	0	0	0	2	2	0	0	0	0	0	0	0	0	0	0
GFVN	0	0	0	0	1	2	0	0	0	2	0	0	2	0	0	0	0
DRKR	0	0	0	0	1	2	1	0	0	1	0	0	4	1	0	0	1
GFCP	0	0	0	0	1	3	0	1	0	1	1	0	6	0	1	0	0
GRGF	0	1	0	2	2	8	0	1	0	1	2	0	8	2	1	0	0

Winter – 2016

Site	Fluoroquinolone			Macrolide					Sulfonamide					Tetracycline			Other
	CIP	OFL	MOX	AZI	CLA	ERY	ROX	TYL	SCM	SDM	SDD	SMR	SMX	DC	MTC	OTC	SIL
POBR	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
BARN	0	0	0	0	0	0	0	0	0	0	0	0	1	2	1	0	0
GFGL	0	0	1	0	0	1	0	0	0	0	0	1	0	0	0	0	0
GFGB	0	0	0	0	0	0	0	0	0	0	0	0	1	2	0	0	0
MCDN	0	0	0	0	0	2	0	0	0	0	0	0	0	2	0	0	0
GFVN	0	0	0	0	0	2	0	0	0	0	0	0	5	0	0	0	0
DRKR	0	0	0	0	0	1	0	0	0	0	0	0	3	0	0	0	0
GFCP	0	0	0	0	0	6	0	0	0	0	0	0	9	0	0	0	0
GRGF	1	1	0	0	0	10	0	0	0	0	0	0	8	1	0	0	0

CIP	Ciprofloxacin
OFL	Ofloxacin
MOX	Moxifloxacin
AZI	Azithromycin
CLA	Clarithromycin
ERY	Erythromycin
ROX	Roxithromycin
TYL	Tylosin
SCM	Sulfacetamide
SDM	Sulfadimethoxine
SDD	Sulfadimidine
SMR	Sulfamerazine
SMX	Sulfamethoxazole
DC	Doxycycline
MC	Meclocycline
MTC	Methacycline
OTC	Oxytetracycline
SIL	Sildenafil

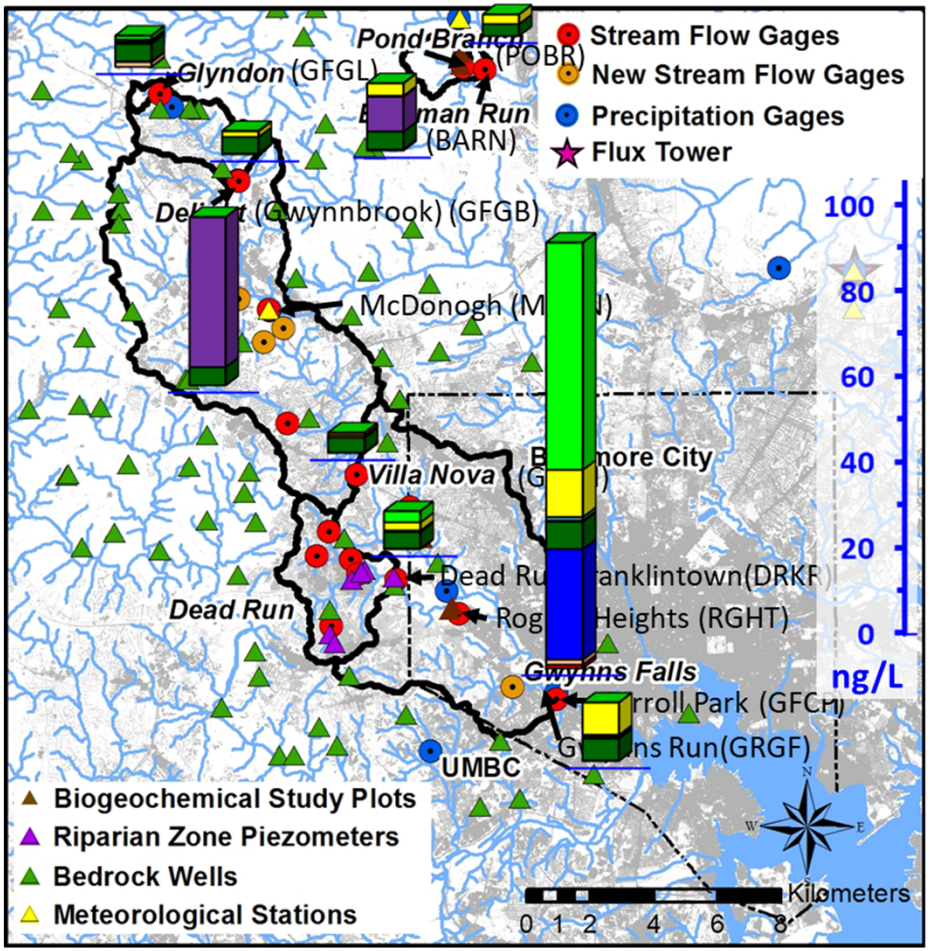
[He *et al.*, in prep]

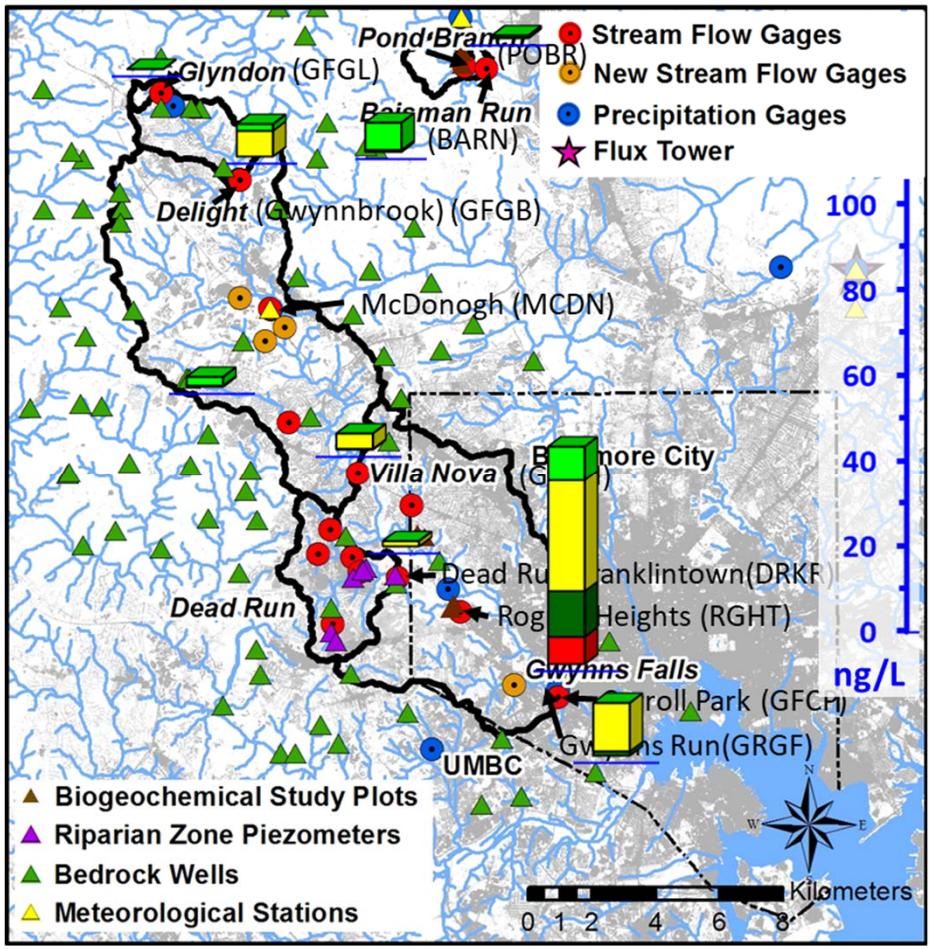
Visualizing antibiotic levels in Gwynns Falls watershed

Summer mean*

Winter mean*

[He *et al.*, in prep]





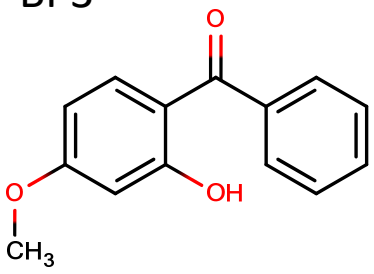
Ofloxacin | Azithromycin | Clarithromycin | Erythromycin | Roxithromycin

Tylosin | Sulfadimethoxine | Sulfadimidine | Sulfamethoxazole | Doxycycline

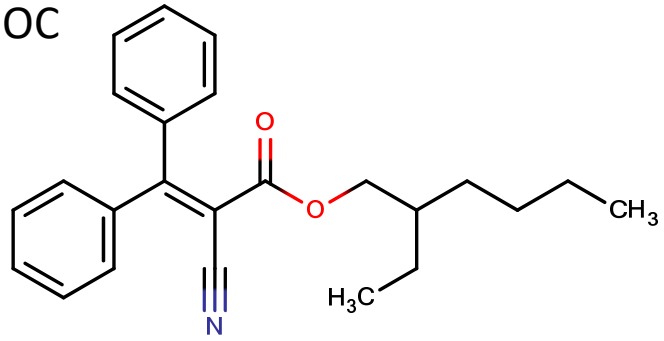
UV-filters are widely present in Gwynns Falls water

Compound	Detection frequency (%)	Maximum concentration (ng/L)
17α-ethinylestradiol	-	-
Estradiol	-	-
Estrone	41.4	6.4
Oxybenzone	**100**	**251**
4-Methylbenzylcathinone	1.2	31
Octocrylene	**100**	**168**
Ethylhexylmethoxycinnamate	68	161
Homosalate	**98**	**314**

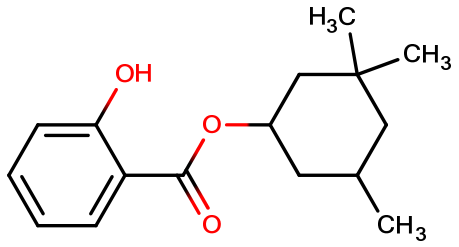
BP3



OC



HMS



[He *et al.*, in prep]

Estrogens and hormones accumulate in urban crayfish

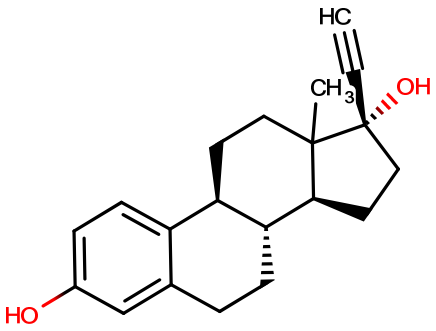
Table 2
Concentrations (ng/g lyophilized tissue) of analytes in the tissue of aquatic organisms. Error is standard deviation (n = 3).

[He *et al.*, 2017]

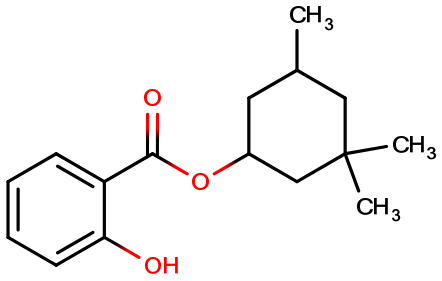
Organism	Site[a]	EE2	E2	E1	BP-3	4-MBC	OC	EHMC	HMS
Eastern crayfish	BARN	n.d.[b]	n.d.	n.d.	n.d.	214 ± 23	60.6 ± 9.0	63.5 ± 7.2	399 ± 48
	DR1	n.d.	n.d.	n.d.	37.9 ± 4.4	352 ± 12	5.0 ± 0.1	n.d.	113 ± 7
	DR2	n.d.	n.d.	n.d.	n.d.	75.3 ± 11	37.1 ± 3.9	83.0 ± 5.1	263 ± 43
	DR3	n.d.	n.d.	n.d.	51.4 ± 2.2	97.8 ± 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



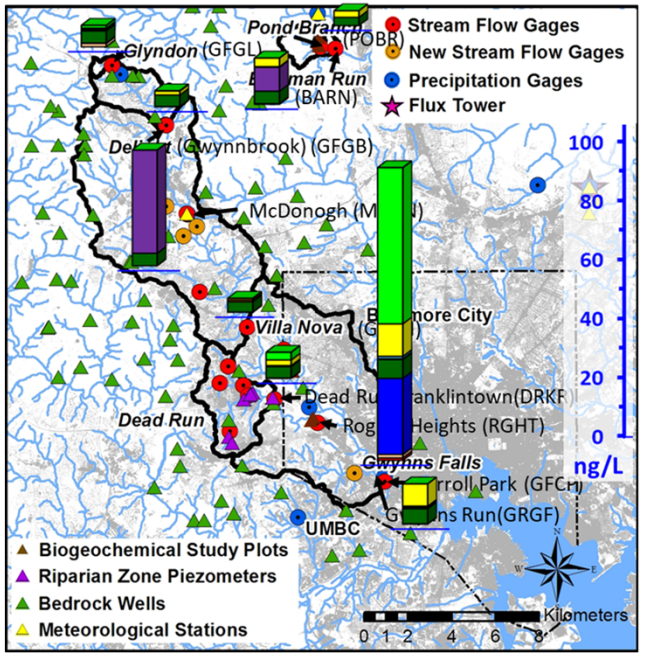
Conclusions

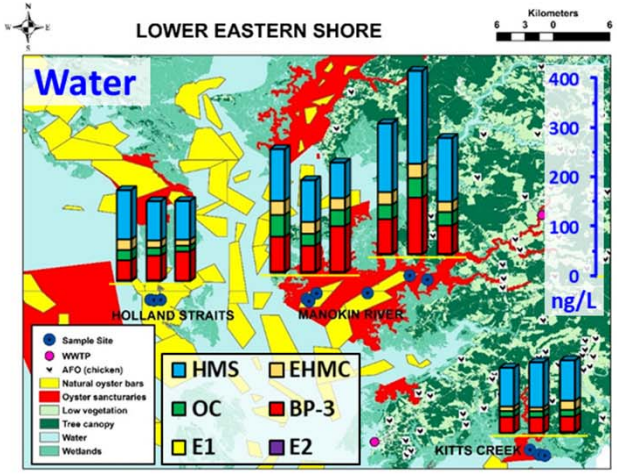
Concluding thoughts

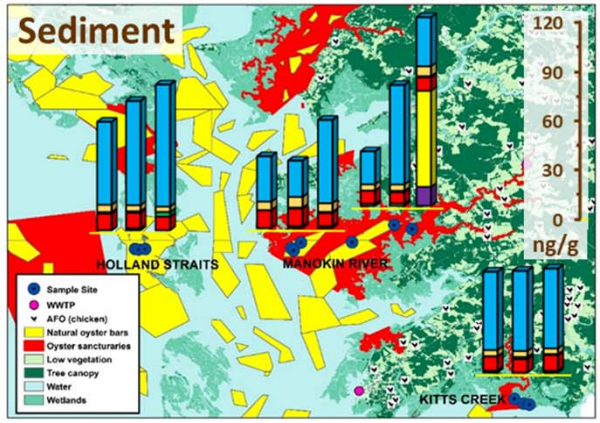
1. Our work in the Gwynns Falls watershed shows that nonpoint (or unexpected) sources can be significant inputs of CECs in urban watersheds

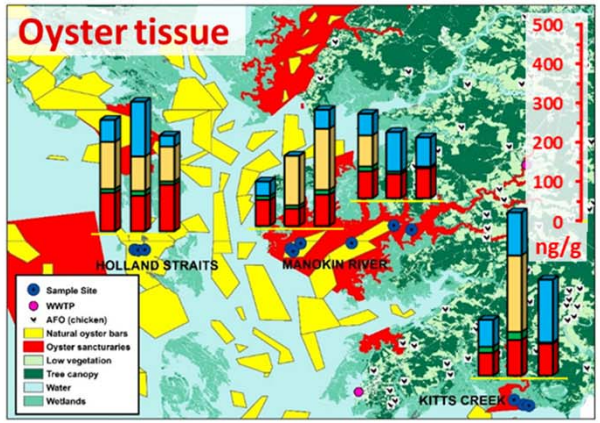
2. CECs are widely present in Chesapeake Bay water, sediment, and oysters and more monitoring studies are required to better understand spatiotemporal trends

3. As CECs were specifically designed to cause biological response, coupled chemical-response studies should be conducted to investigate unexpected toxicity









My great team


Lee Blaney


Ke He


Utsav Shashvatt


Temitope Ibitoye


Mamatha Hopanna


Ethan Hain


Charles Portner


Samina Musa


Savannah Steinly


Josh Benoit


Hannah Aris

A special thanks to our funding sources

Environmental Protection Agency, P3 program
Maryland Industrial Partnerships
Maryland Department of Natural Resources
Maryland Sea Grant
National Science Foundation, CAREER program
National Science Foundation, Environmental Engineering program
National Science Foundation, Environmental Sustainability program
National Science Foundation, Environmental Chemical Sciences program
National Science Foundation, INFEWS N/P/H2O program
Personal Care Products Council
UMBC Office of Undergraduate Education
UMBC Office of the Vice President of Research
US-Israel Binational Agricultural Research and Development Fund
USDA Forest Service

Thanks for your attention

Any questions?

Lee Blaney

Department of Chemical, Biochemical and Environmental Engineering

University of Maryland Baltimore County

410-455-8608

blaney@umbc.edu

www.umbc.edu/blaneylab