

Sources and occurrence of contaminants of emerging concern and the risk they pose to the Chesapeake Bay

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My goals for today

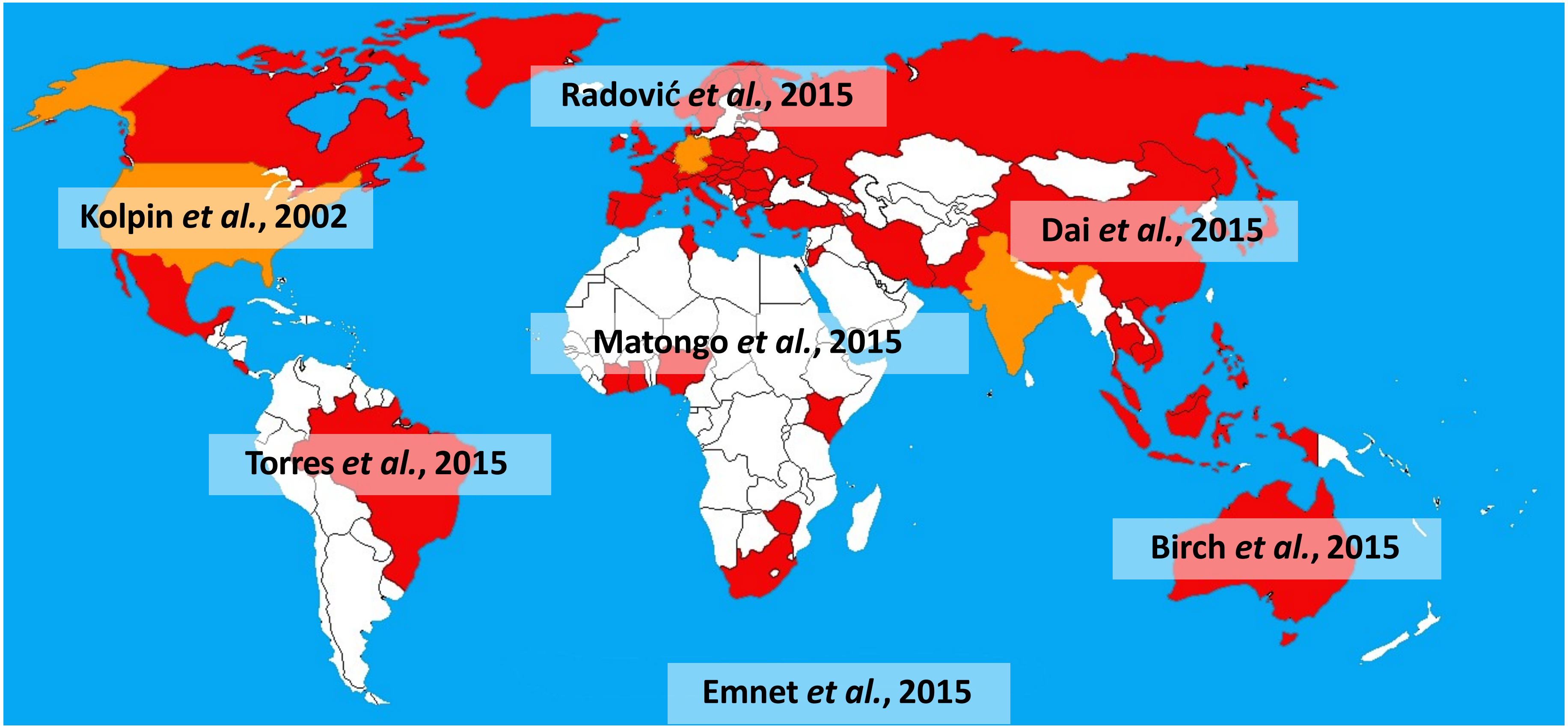
1. To provide an overview on contaminants of emerging concern (CECs) and **identify priority CECs**

2. To describe **analytical methods** used to measure trace concentrations of CECs in complex environmental matrices

3. To discuss our recent work on **detection of CECs** in
   i. the Chesapeake Bay;
   ii. urban watersheds; and,
   iii. wastewater treatment plants

Overview

CECs are present in water around the world



Priority* CECs – endocrine disruptors

Estrogenic hormones – signaling molecules that affect reproductive systems; can impact aquatic organisms at concentrations as low as 1-10 ng/L; results in population crashes

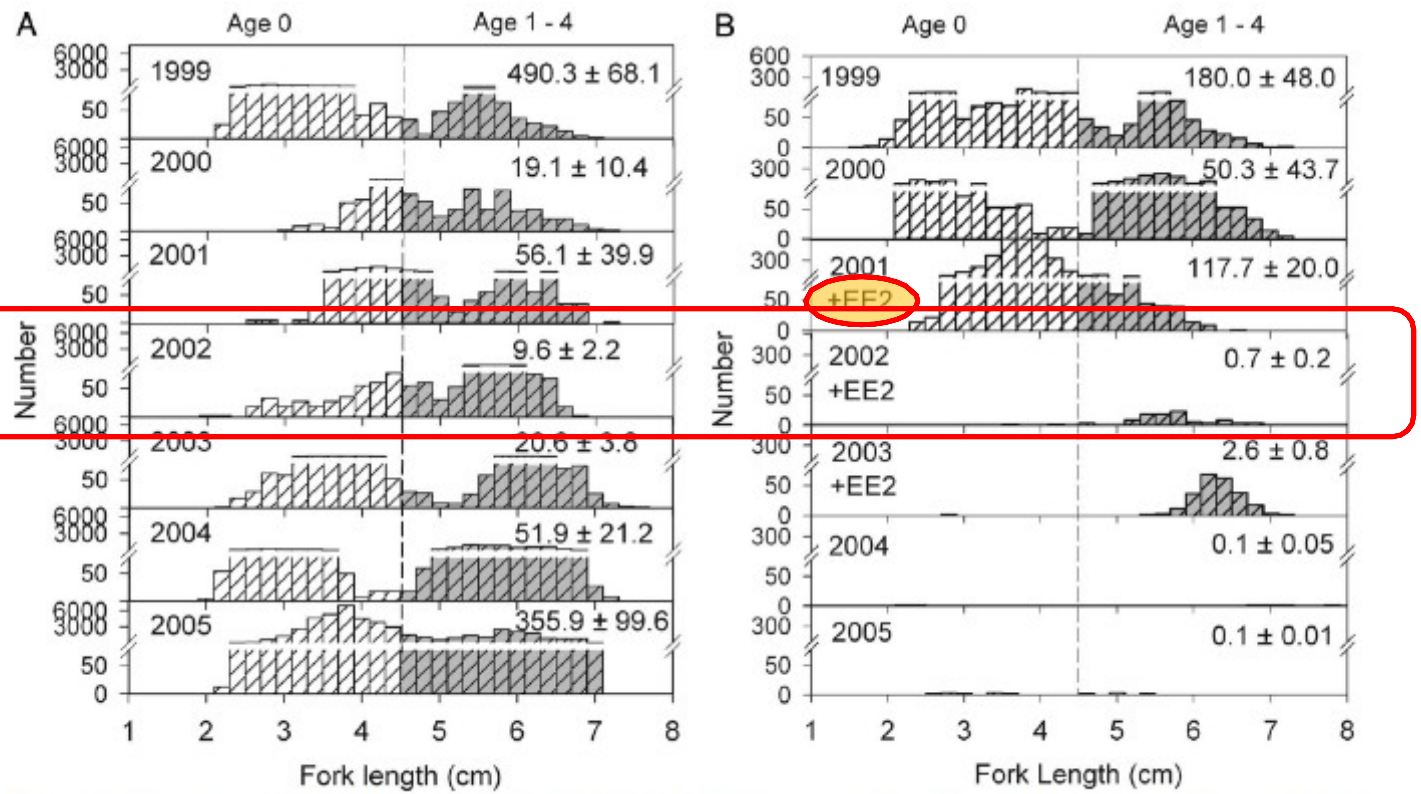


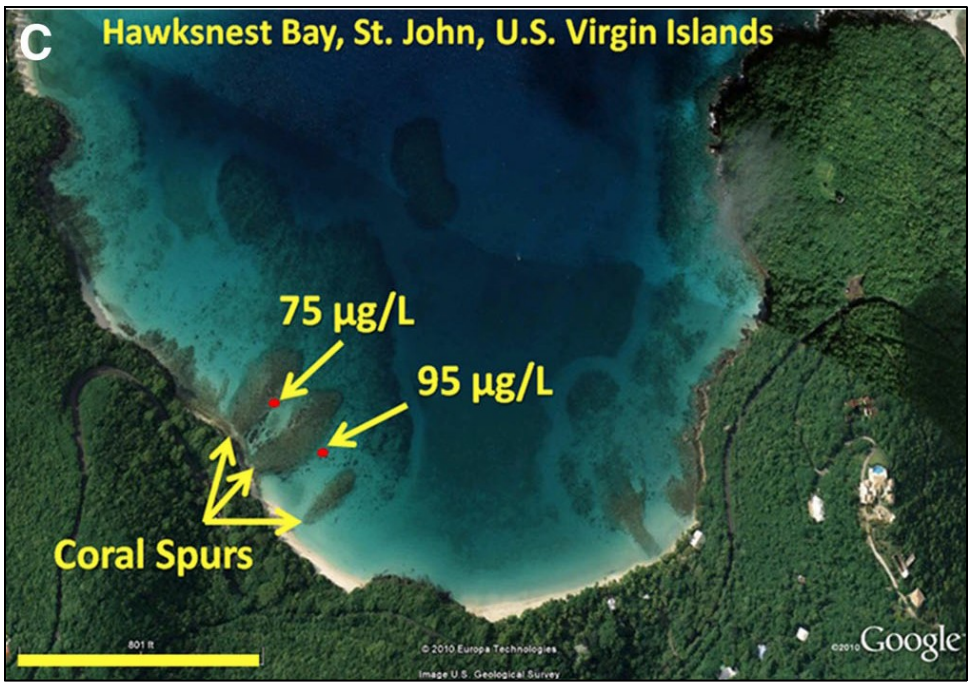
Fig. 3. Length frequency distributions of fathead minnow captured in trap nets in reference Lake 442 (*A*) and Lake 260 (*B*) (amended with 5–6 ng·L⁻¹ of EE2 in 2001–2003) during the fall of 1999–2005. Distributions for each fall have been standardized to 100 trap-net days. Mean ± SE daily trap-net CPUE data for adults and juveniles for the fall catches are shown in the panels.

[Kidd *et al.*, 2007]

Priority* CECs – genotoxic personal care products

UV-filters – these molecules are present in most personal care products (high loads); UV-filters exhibit estrogenic activity; recently shown to be toxic to corals at < 100 ng/L

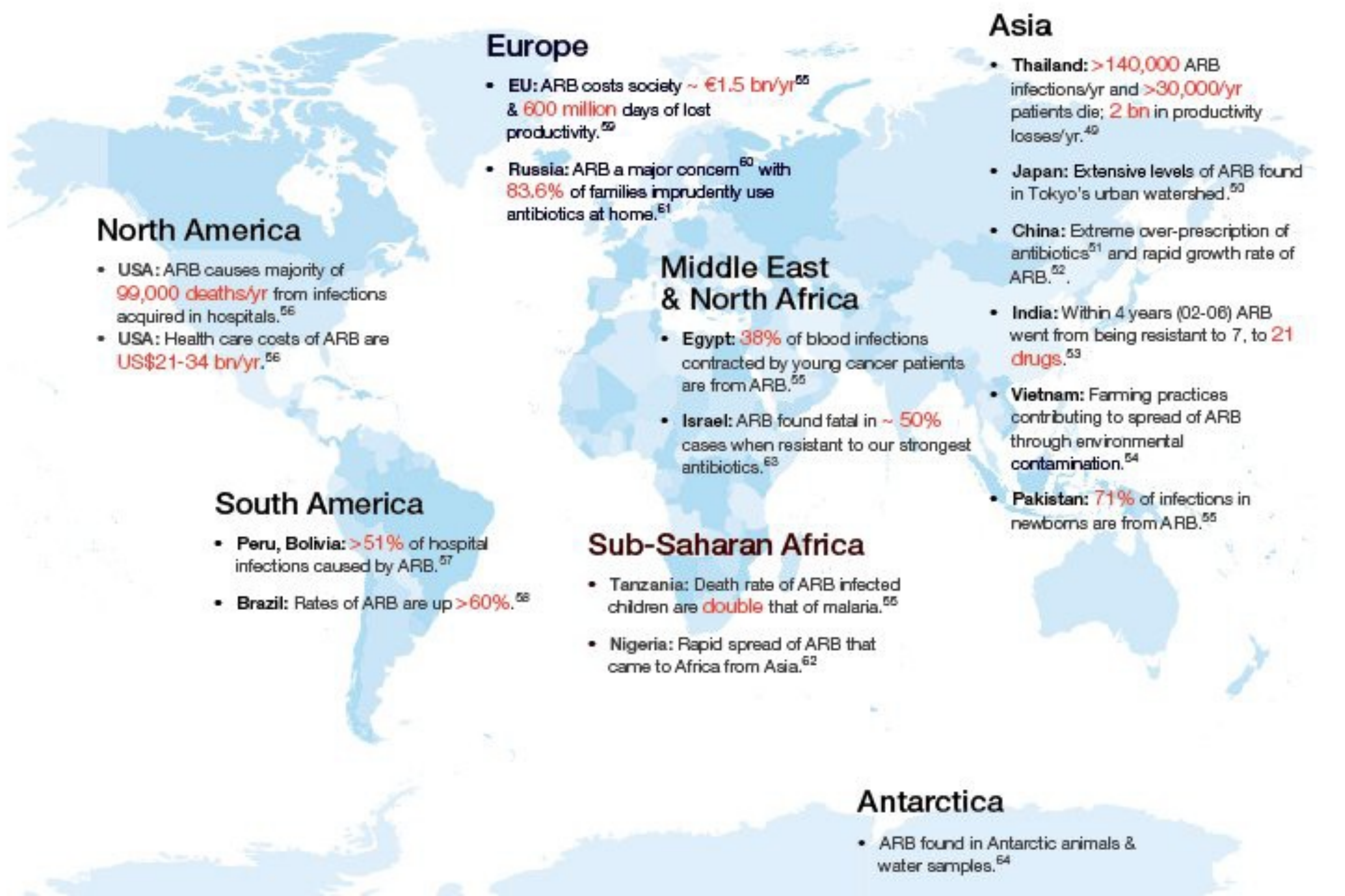
"Oxybenzone poses a hazard to coral reef conservation and threatens the resiliency of coral reefs to climate change." [Downs *et al.*, 2015]



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

Priority* CECs – a grand public health challenge

Antibiotics – sub-therapeutic concentrations of antibiotics elicit cell-signaling responses; environmentally-relevant levels of antibiotics exert a selective pressure for resistant organisms



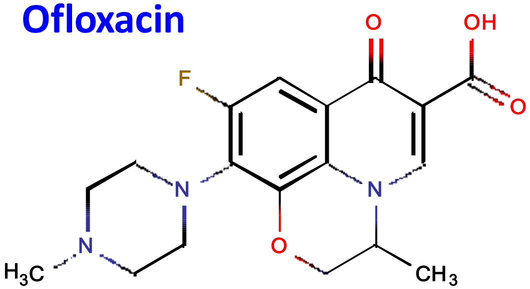
[WEF, 2013]

Analytical Methods

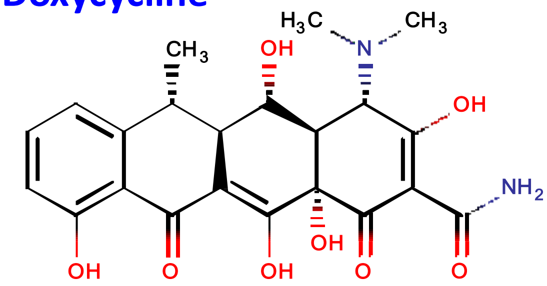
We measure a large suite of CECs…

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

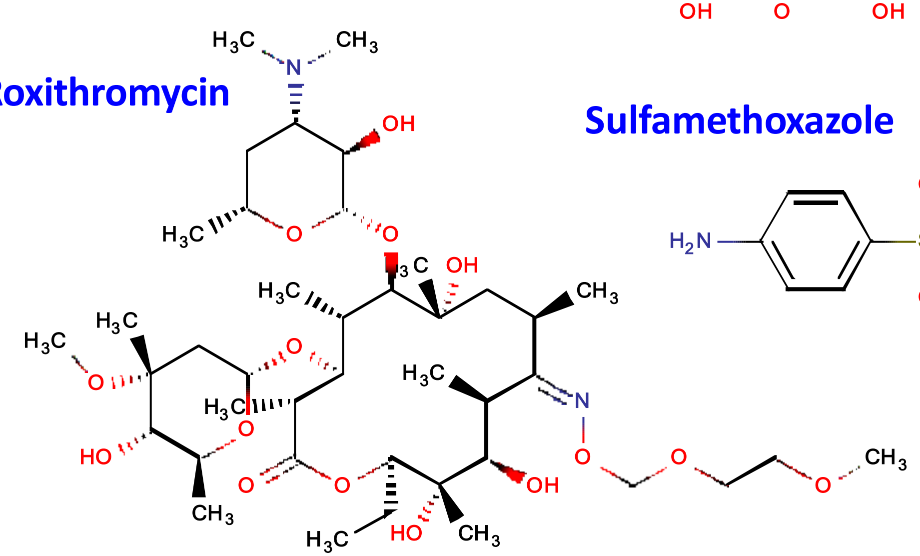
Ofloxacin



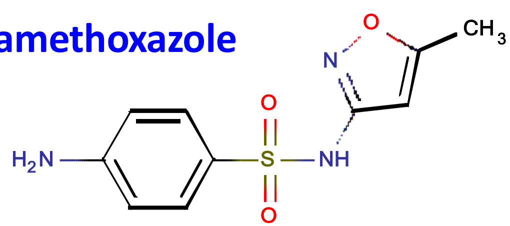
Doxycycline



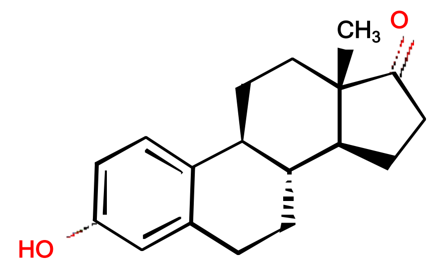
Roxithromycin



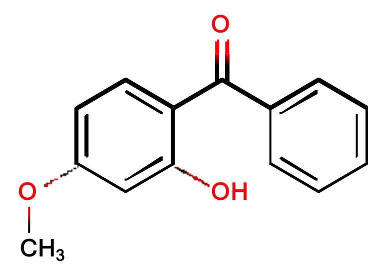
Sulfamethoxazole



Estrone



Oxybenzone

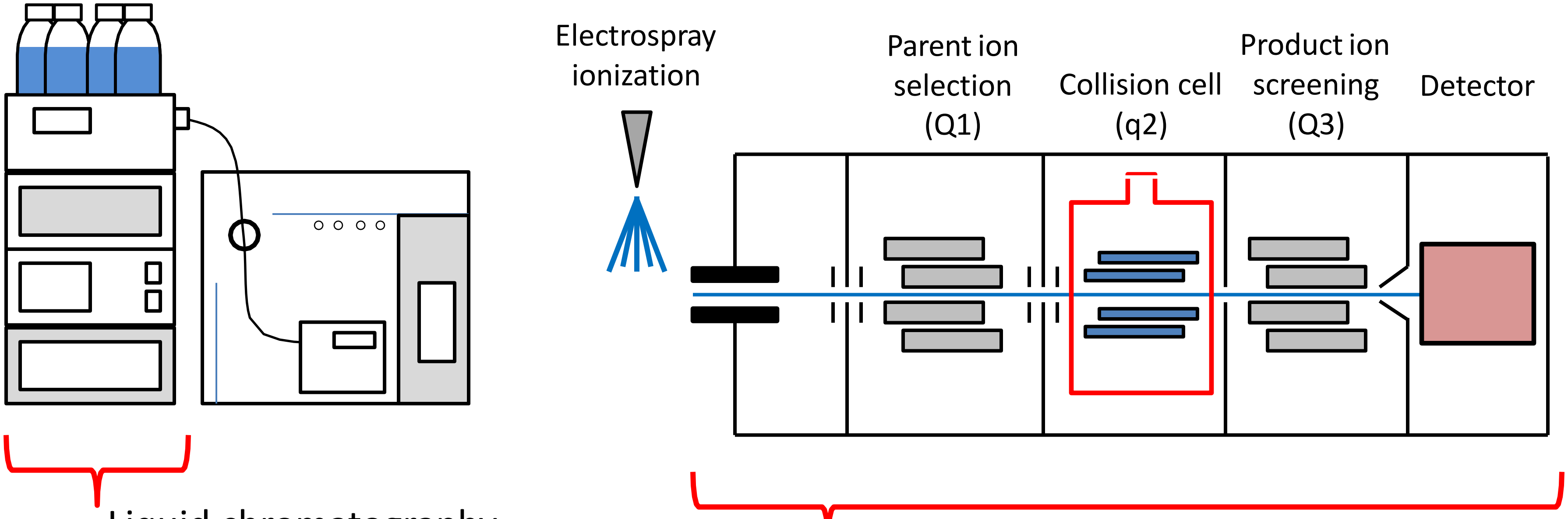


Sample pretreatment with Solid-Phase Extraction (SPE)

SPE serves two dominant purposes:

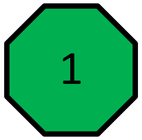
- Remove interferences
- Concentrate analytes

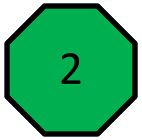
SPE with LC-ESI-MS/MS

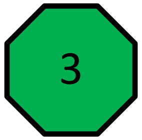


Liquid chromatography
(separates analytes)

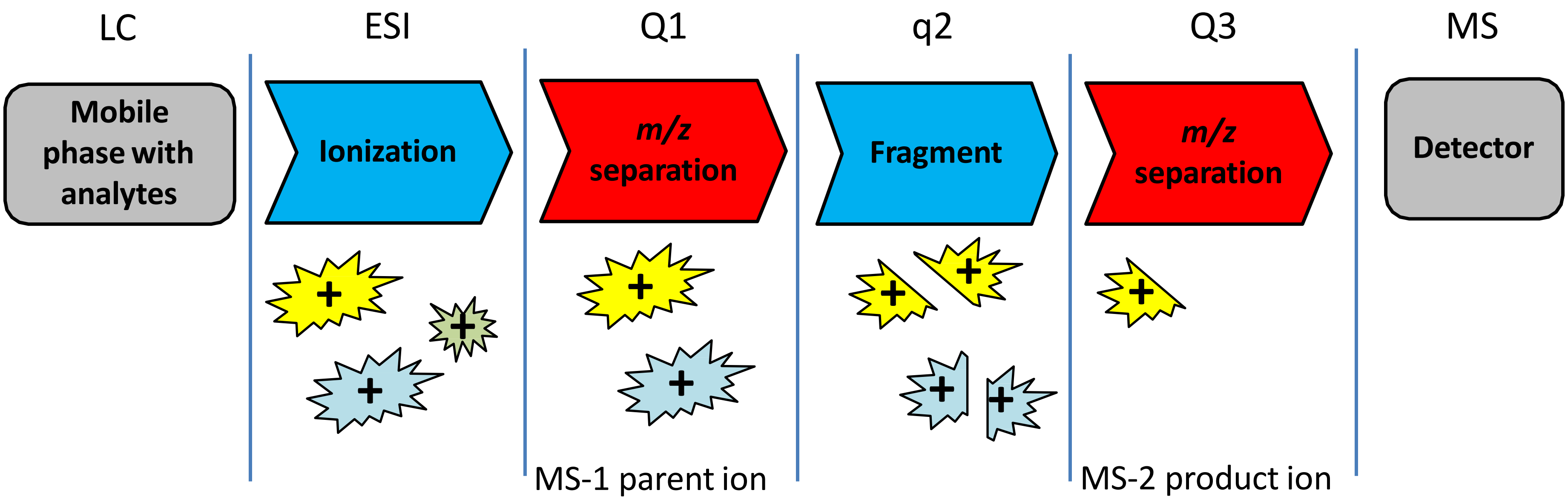
Tandem mass spectrometry
(detects analytes)







Tandem MS provides high selectivity/sensitivity

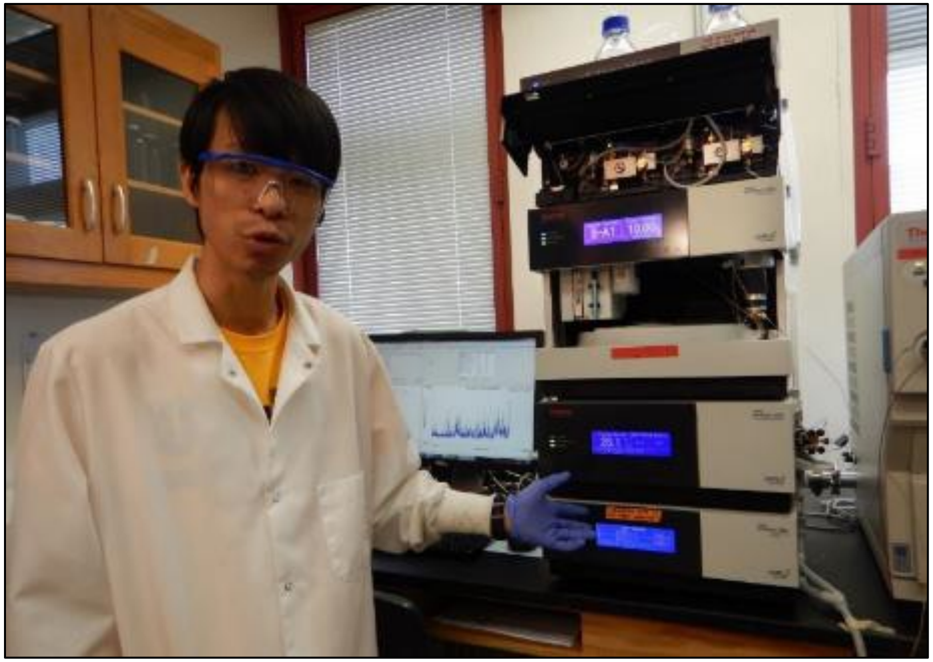


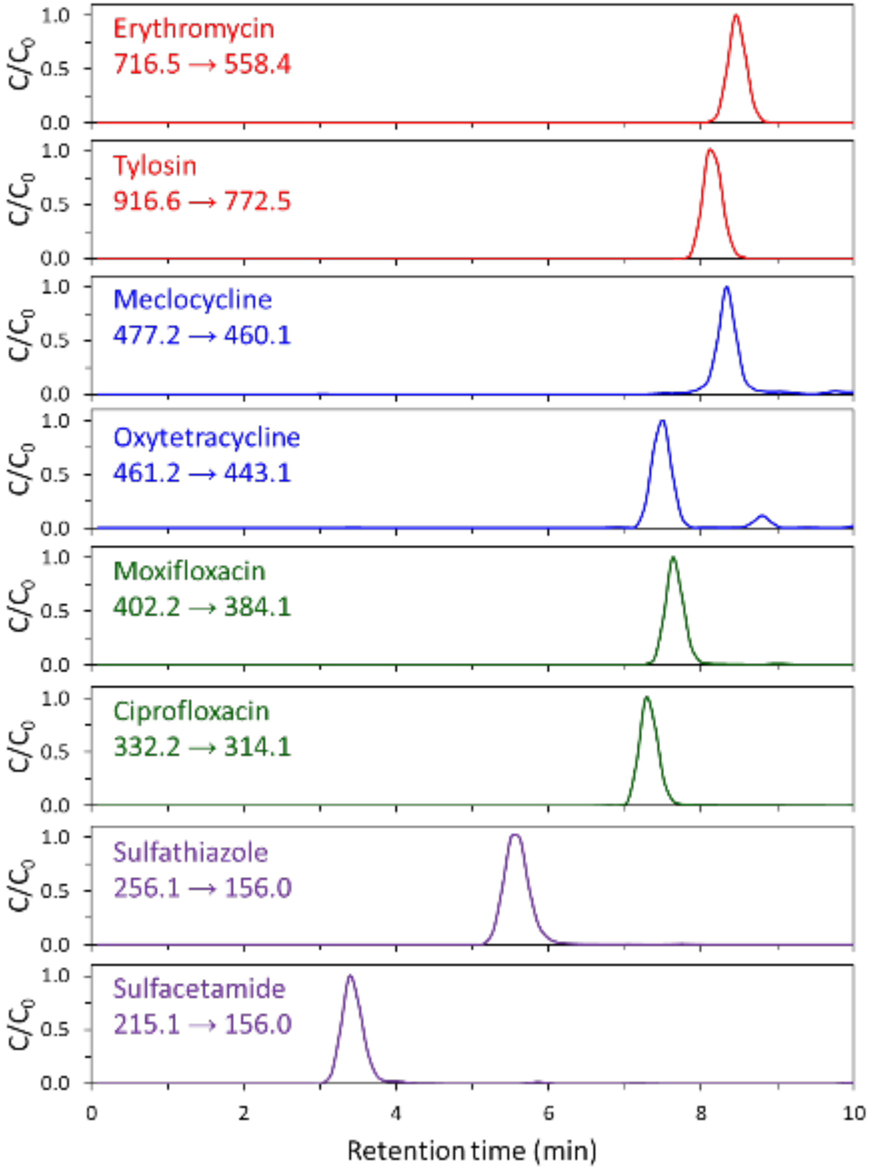
- MS/MS detection methods measure the transition from [MS-1] to [MS-2]
- Minimal noise/interference from other species (compared to bulk detectors)

Now measuring 60-70 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).

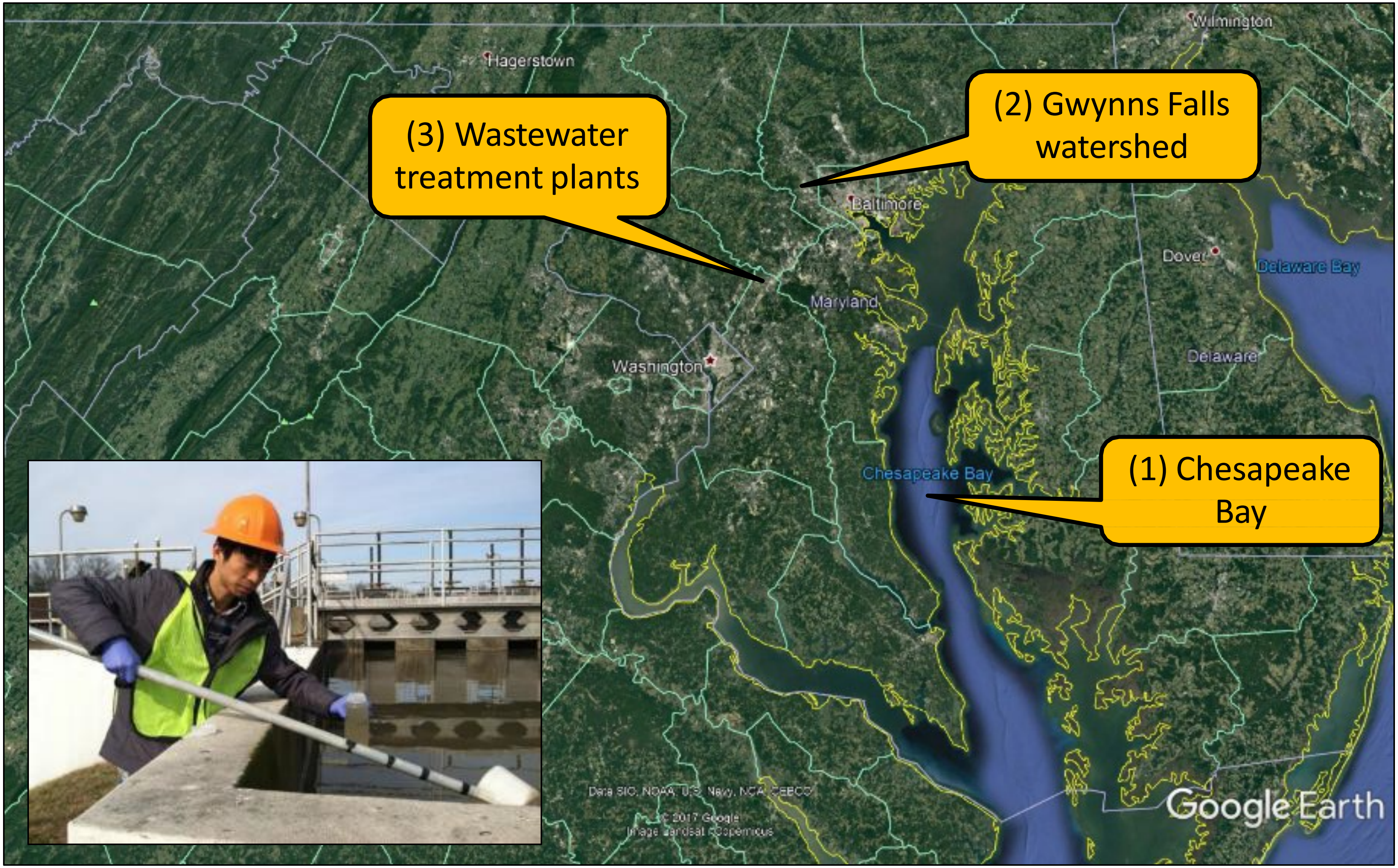
Limits of detection ≤ 1.5 ng/L





Sources of CECs

Occurrence of CECs in Maryland

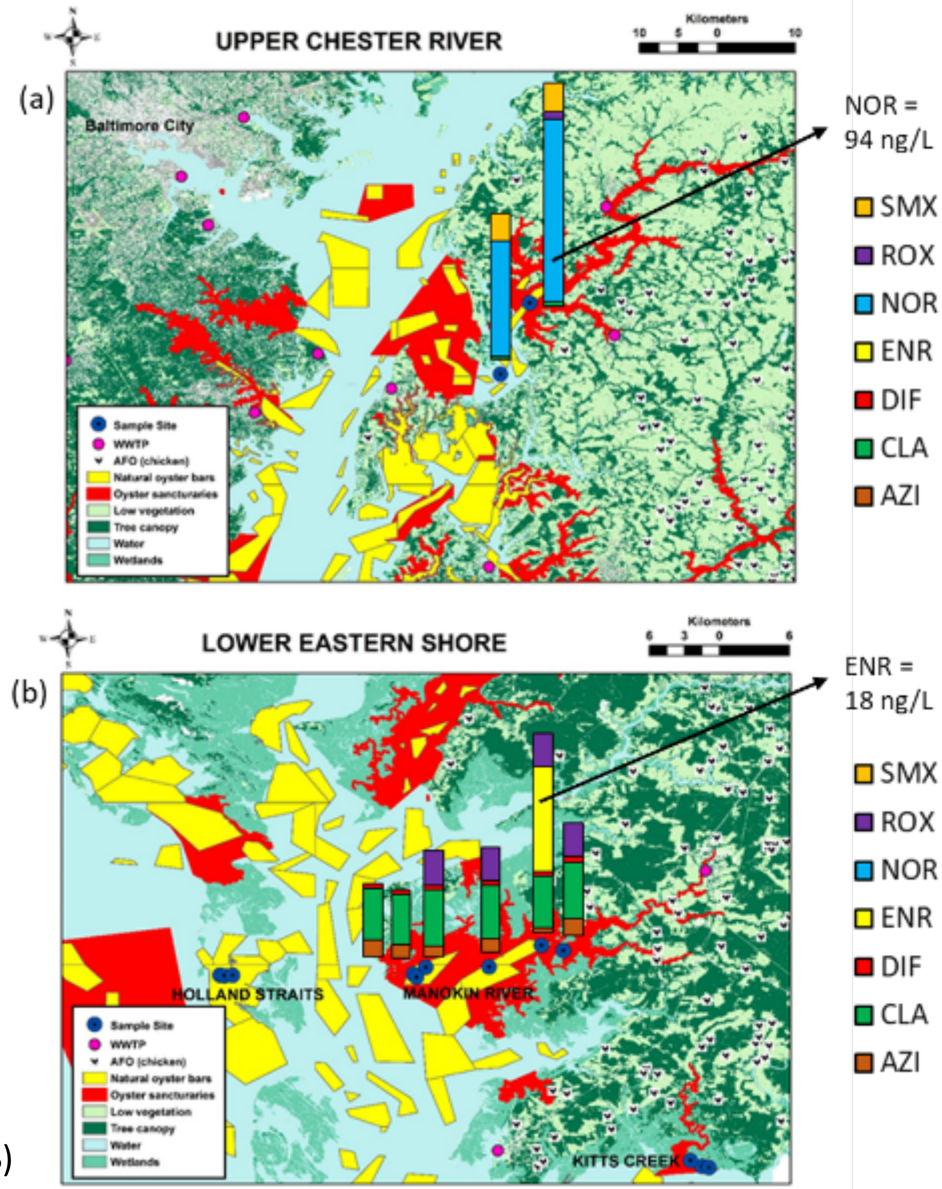


Hypothesis

CECs are present in the Chesapeake Bay and accumulate in oyster tissue

Antibiotics in the Chesapeake Bay

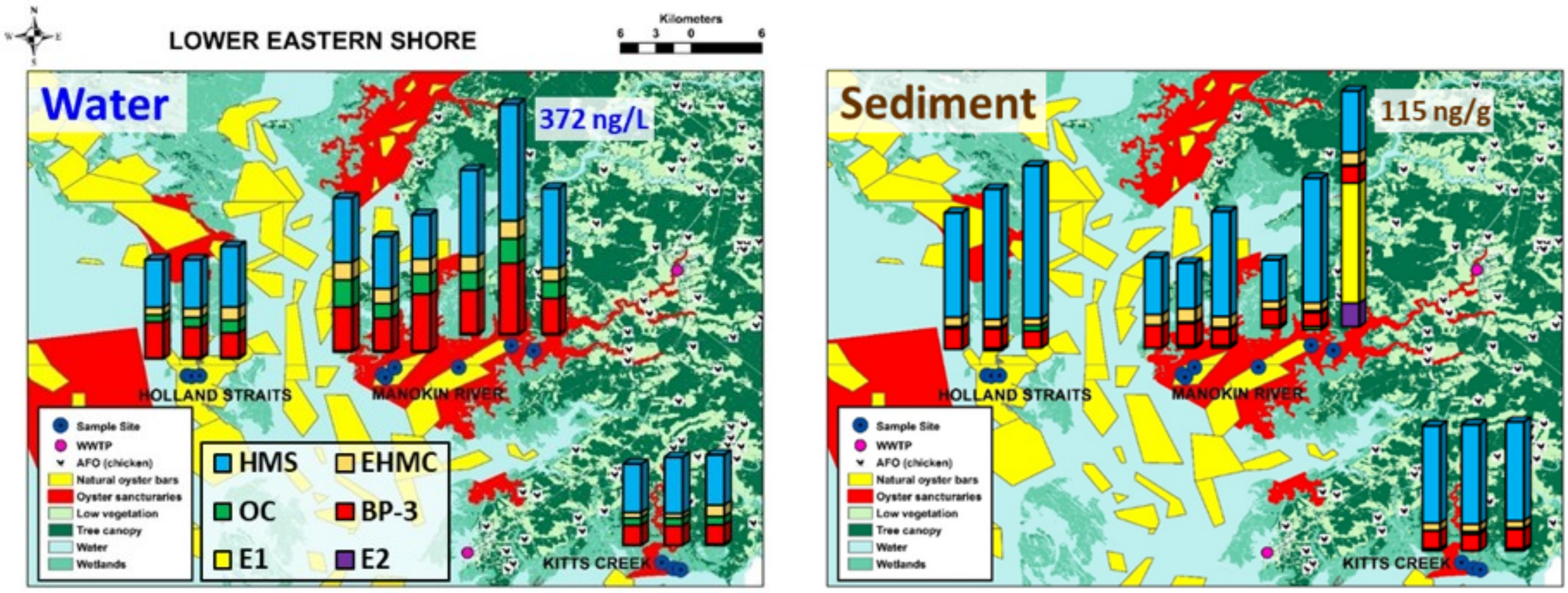
Compound	Max. conc. (ng/L)
Azithromycin (AZI)	2.7 ± 0.5
Clarithromycin (CLA)	9.7 ± 0.6
Difloxacin (DIF)	0.9 ± 0.1
Enrofloxacin (ENR)	17.8 ± 1.3
Norfloxacin (NOR)	94.1 ± 28.1
Roxithromycin (ROX)	5.9 ± 0.0
Sulfamethoxazole (SMX)	14.8 ± 3.8



Map credit: Anne Timm (USFS)

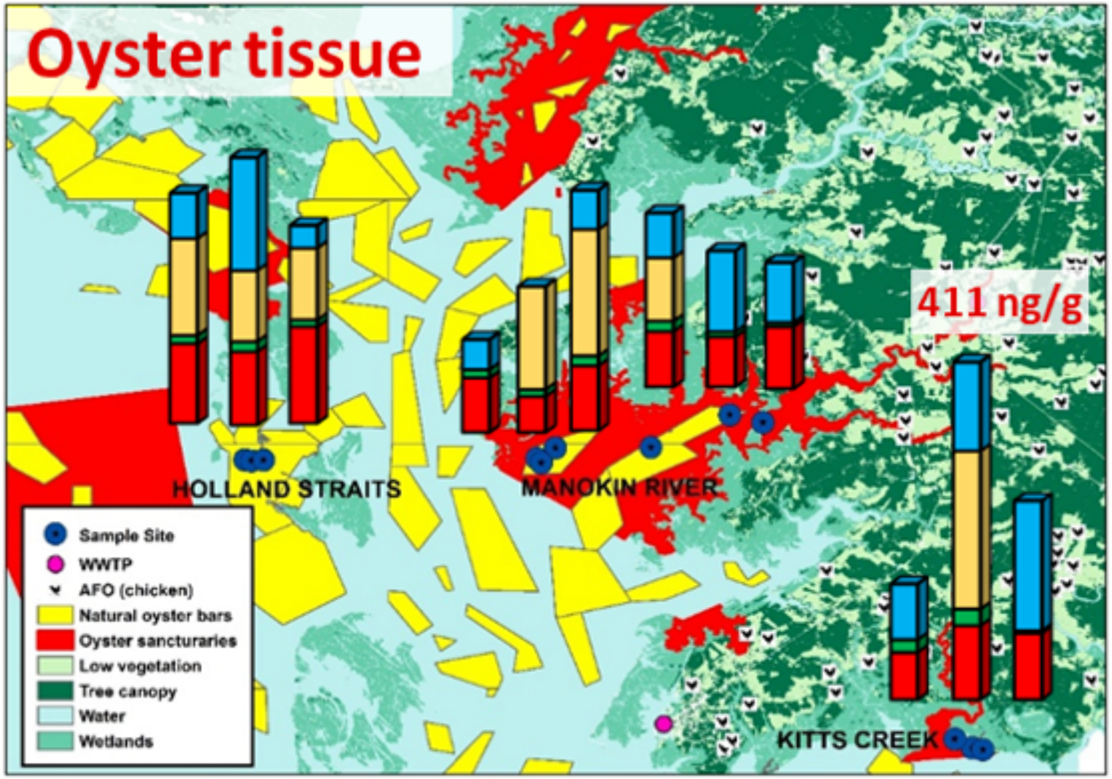
UV-filters and estrogenic hormones in the Chesapeake Bay

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



Map credit: Anne Timm (USFS)

CECs accumulate in Chesapeake Bay oysters



Map credit: Anne Timm (USFS)

Current Chesapeake Bay sampling campaign

Sampling done in conjunction with MDNR

“We get what we measure”

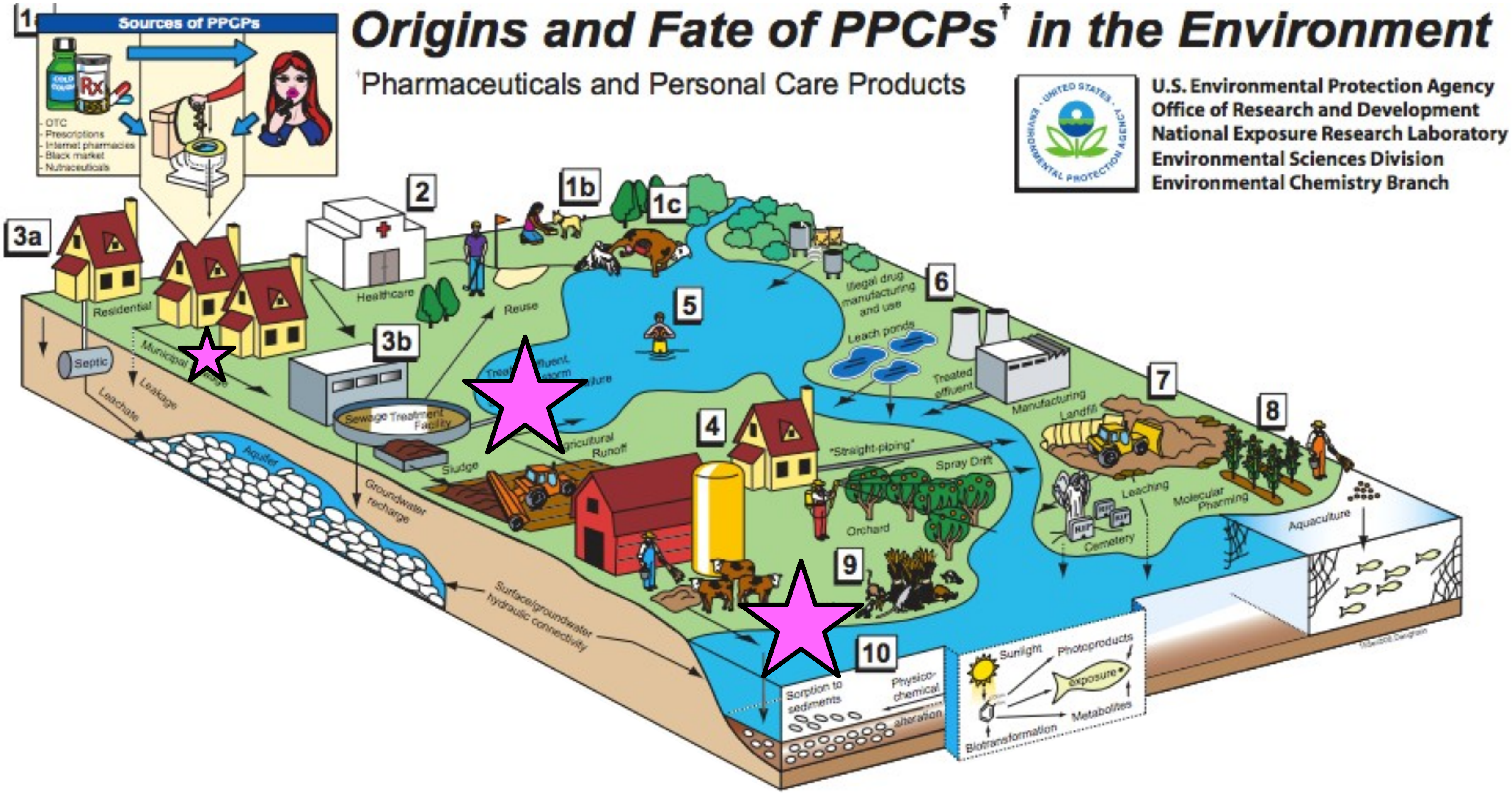
<u>Sampling campaigns for CECs focus on expected sites</u>

- Kolpin *et al.*, 2002 – “the selection of sampling sites primarily *focused on areas considered susceptible to contamination* from human, industrial, and agricultural wastewater.”

- Barnes *et al.*, 2008 – “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).”

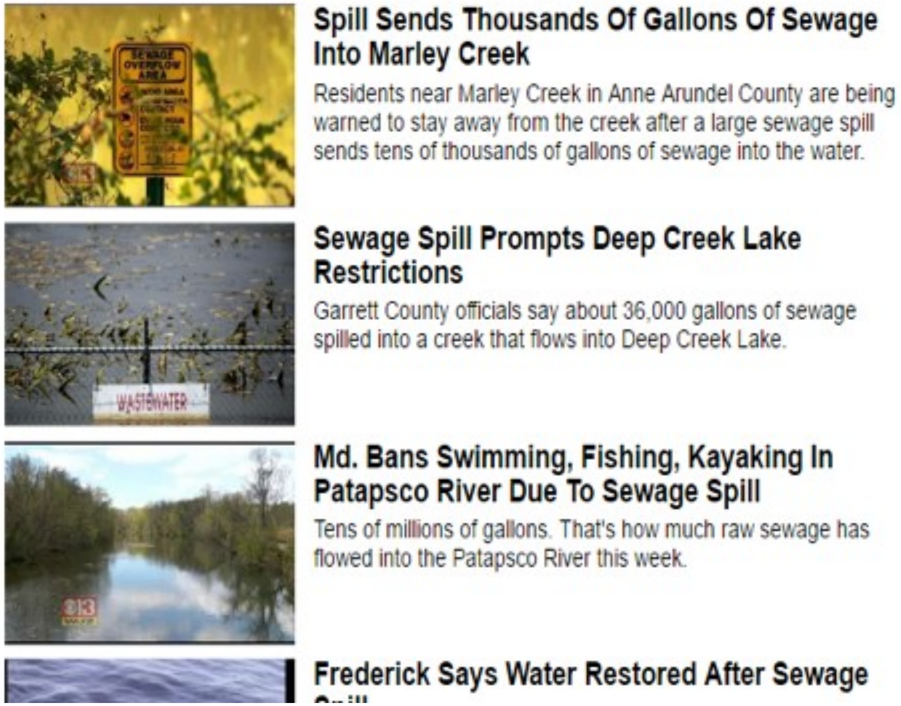
There have been few efforts conducted in “unimpacted” streams and watersheds.

Sources of CECs – revisiting assumptions



Wastewater leaks are common occurrences

The 2004 water quality management plan stated, “Sewage discharge into the Gwynns Falls is a major concern…Many sections of the stream…are posted due to contaminated streamflow… <u>Continuous sewer leaks are common occurrences in Baltimore City</u>”.



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.

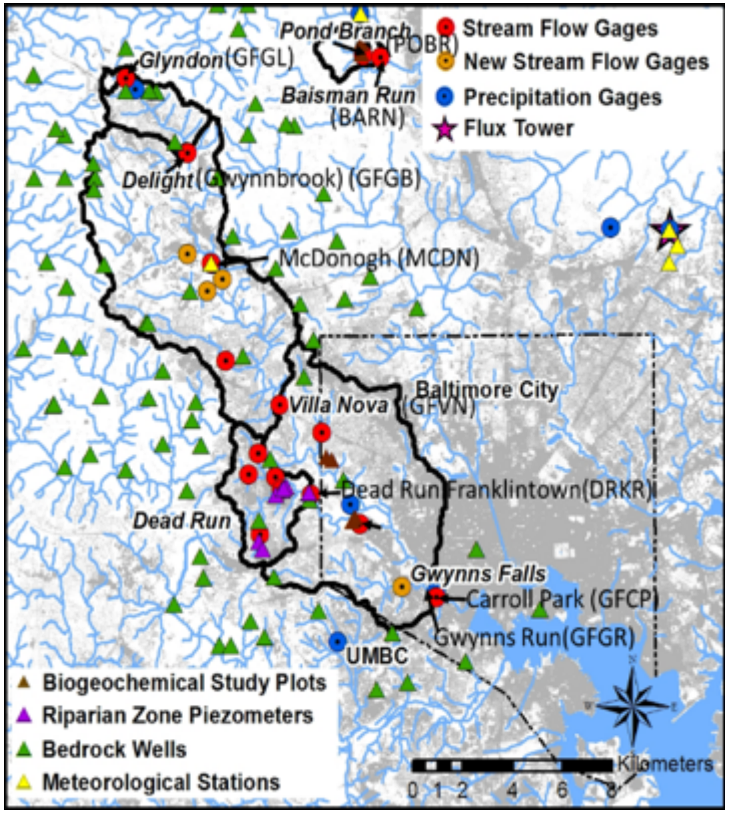
Frederick Says Water Restored After Sewage

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…

Hypothesis

CECs are present in Maryland surface waters due to leaking sewer systems

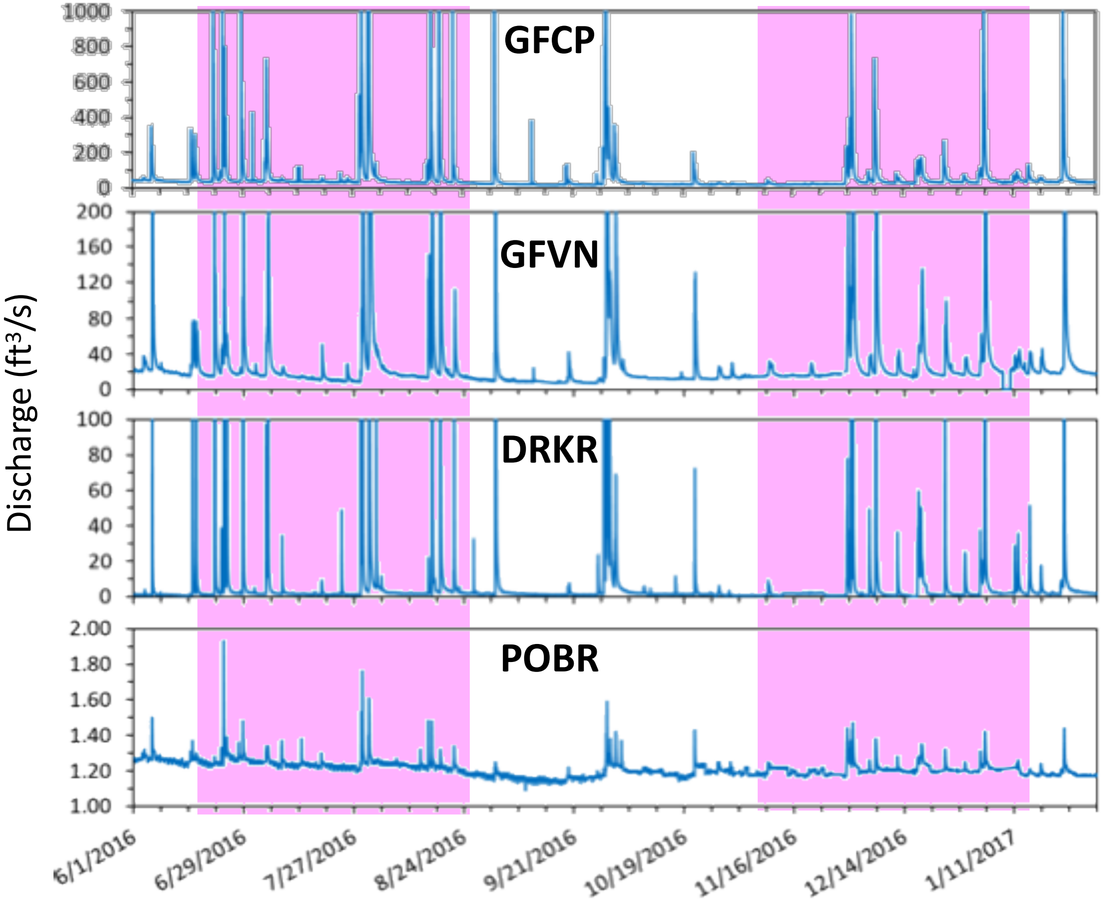
We sampled *unimpacted* urban streams



Source: Baltimore Ecosystem Study

Summer sampling
6/15/16 – 08/26/16

Winter sampling
11/8/16 – 01/12/17

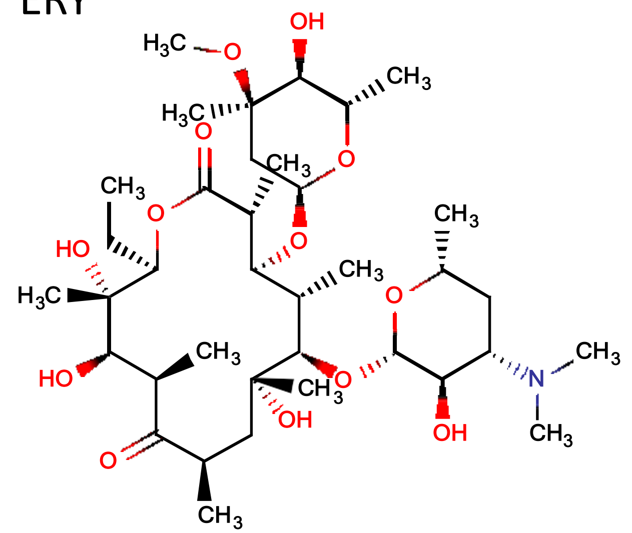


Source: USGS NWIS

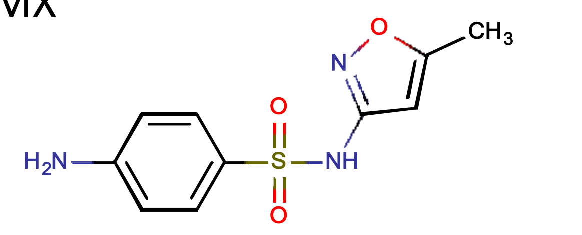
A wide variety of antibiotics were detected in water

Compound	Detection	Maximum
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



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

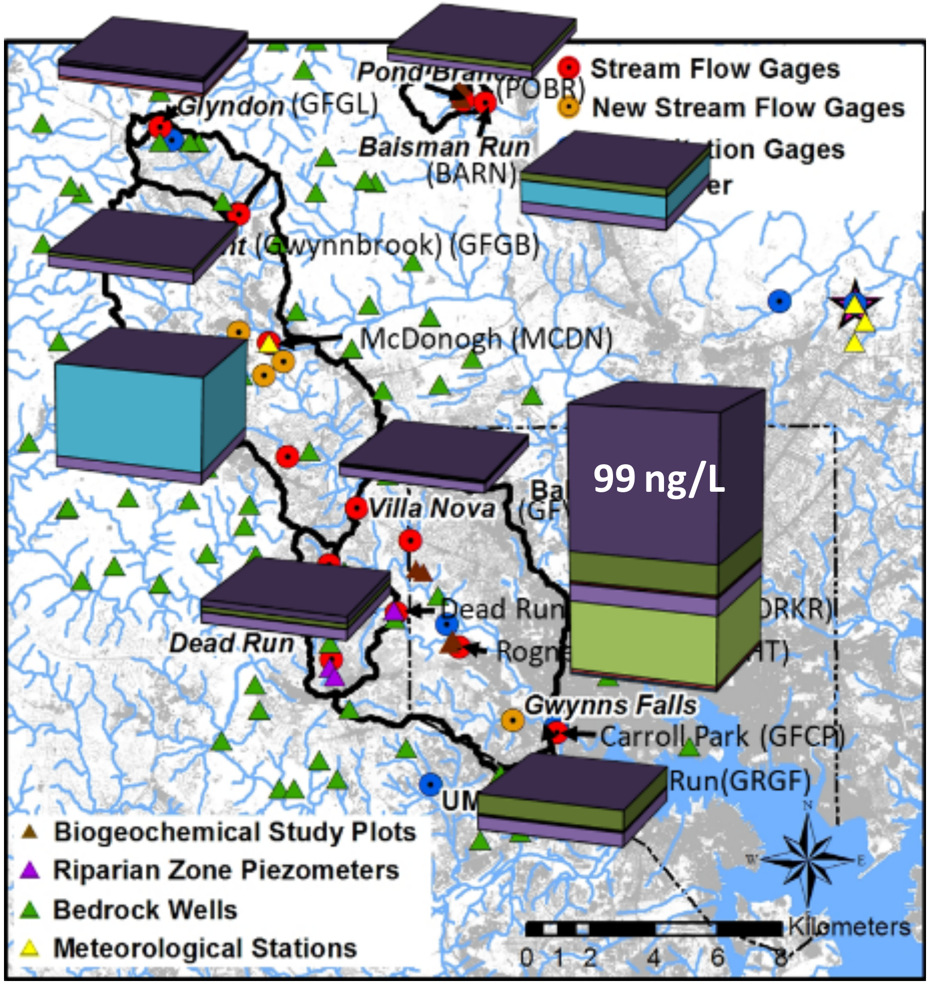
Winter – 2016

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

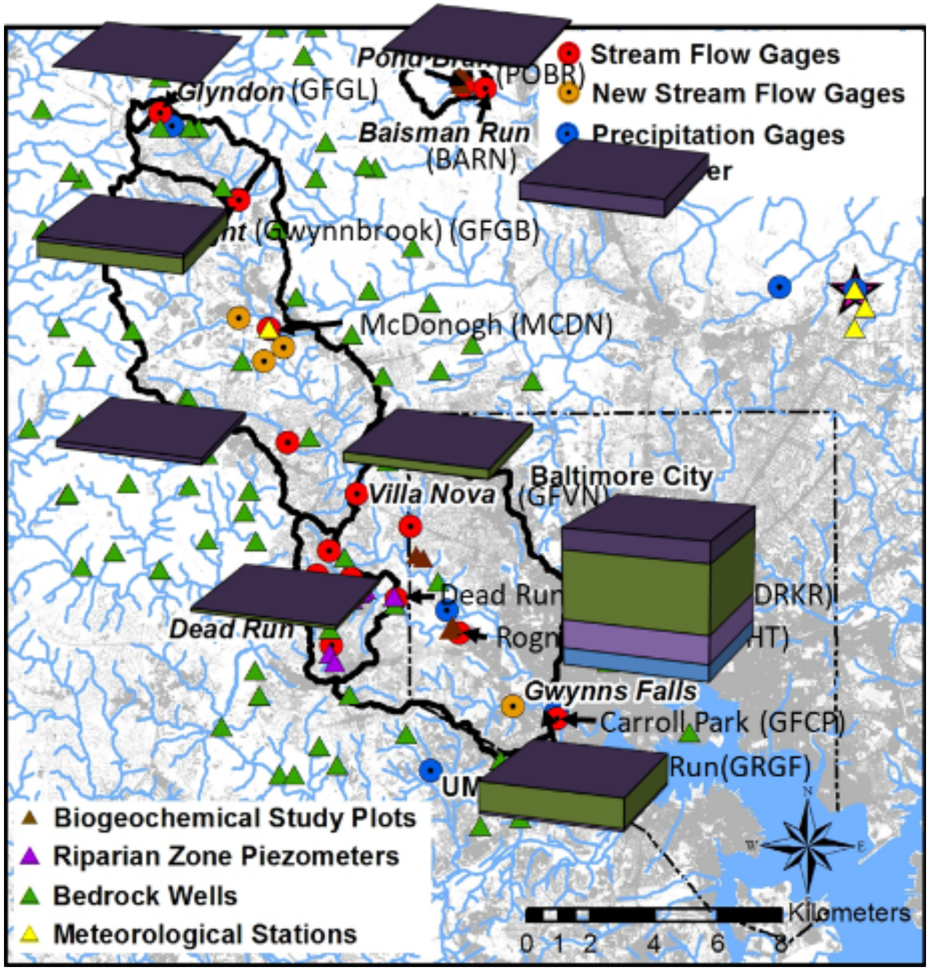
CIP	Ciprofloxacin
OFL	Ofloxacin
MOX	Moxifloxacin
AZI	Azithromycin
CLA	Clarithromycin
ERY	Erythromycin
ROX	Roxithromycin
TYL	Tylosin
SCM	Sulfacetamide
SDM	Sulfadimethoxine
SDD	Sulfadimidine
SMR	Sulfamerazine
SMX	Sulfamethoxazole
DC	Doxycycline
MC	Meclocycline
MTC	Methacycline
OTC	Oxytetracycline
SIL	Sildenafil

Mapping antibiotics in Gwynns Falls watershed

Summer mean*



Winter mean*

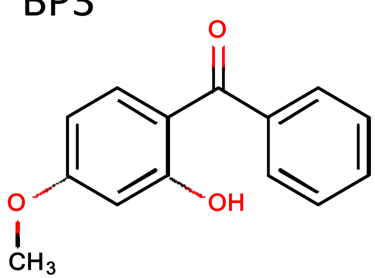


Doxycycline | Sulfamethoxazole | Sulfadimidine | Sulfadimethoxine | Tylosin
Roxithromycin | Erythromycin | Clarithromycin | Azithromycin | Ofloxacin

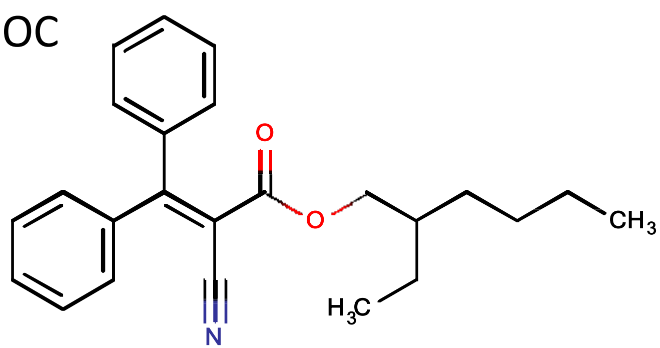
UV-filters are widely present in Gwynns Falls water

Compound	Detection fr)	Maximum conc g/L)
17α-ethinylestradiol	-	-
Estradiol	-	-
Estrone	41.4	6.4
Oxybenzone	**100**	**251**
4-Methylbenzylcathinone	1.2	31
Octocrylene	**100**	**168**
Ethylhexyl methoxycinnamate	68	161
Homosalate	**98**	**314**

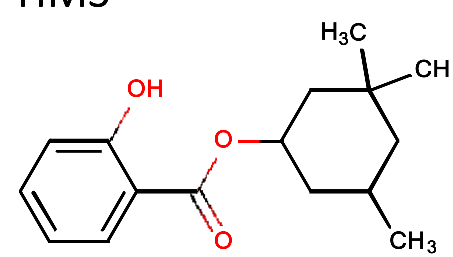
BP3



OC

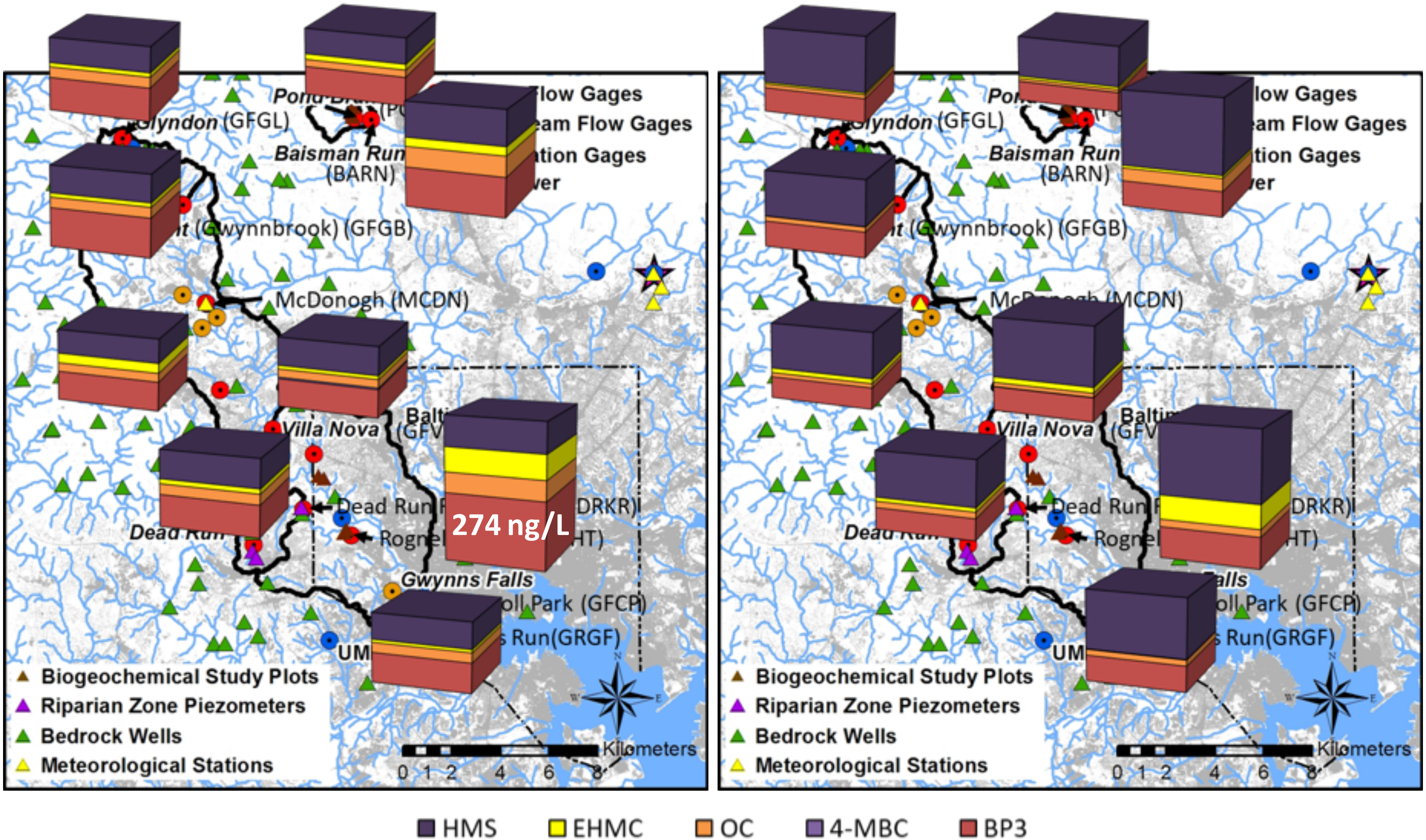


HMS



Mapping UV-filters in Gwynns Falls watershed

Summer mean* **Winter mean***



Estrogens and hormones accumulate in crayfish

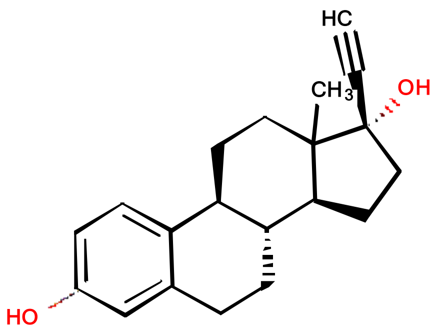
[He *et al.*, 2017]

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

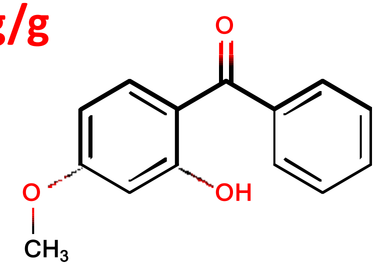
Organism	Site[a]	EE2	E2	E1	BP-3	4-MBC	OC	EHMC	HMS
Eastern crayfish	BARN	n.d.[b]	n.d.	n.d.	n.d.	214 ± 23	60.6 ± 9.0	63.5 ± 7.2	399 ± 48
	DR1	n.d.	n.d.	n.d.	37.9 ± 4.4	352 ± 12	5.0 ± 0.1	n.d.	113 ± 7
	DR2	n.d.	n.d.	n.d.	n.d.	75.3 ± 11	37.1 ± 3.9	83.0 ± 5.1	263 ± 43
	DR3	n.d.	n.d.	n.d.	51.4 ± 2.2	97.8 ±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

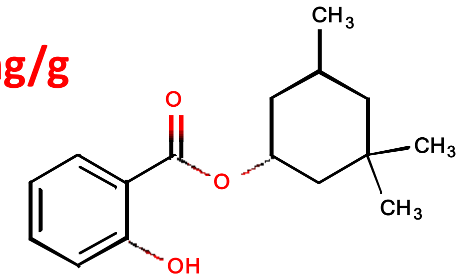
EE2: 17.1 ± 1.6 ng/g



BP3: 23.7±0.3 ng/g



HMS: 399 ± 48 ng/g



Hypothesis

CECs undergo complex transformation reactions in wastewater treatment

Antibiotic concentrations are reduced in WW treatment

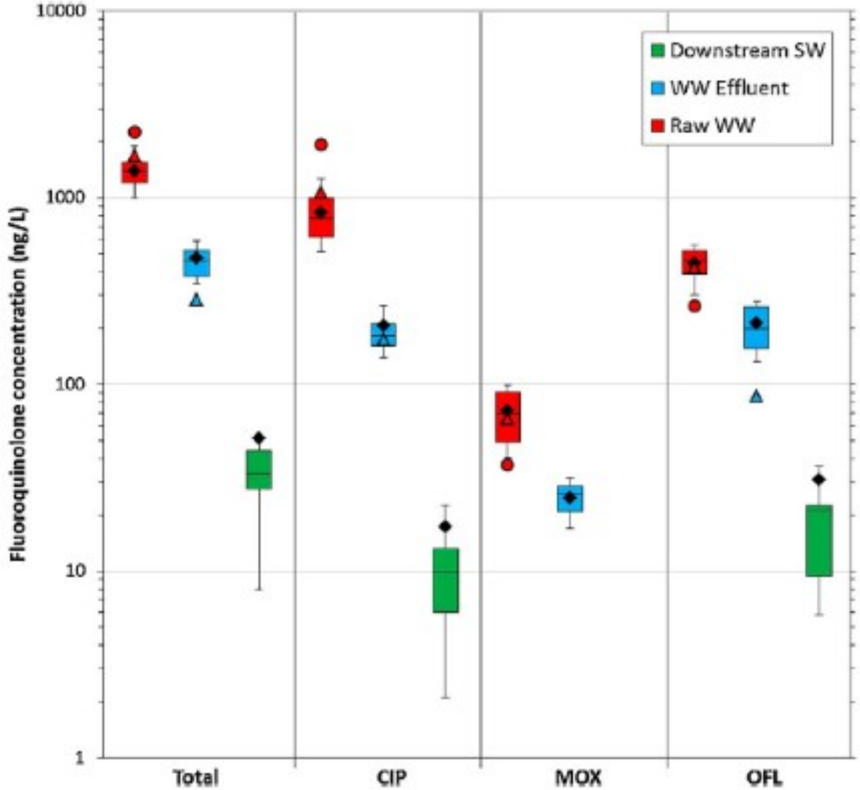


Fig. 2. Box-and-whisker diagram of FQ concentrations in raw wastewater (red), wastewater effluent (blue), and downstream surface water (green). (Black diamonds indicate mean concentrations; triangles indicate FQ concentrations in raw wastewater and wastewater effluent from the large WWTP; circles indicate FQ concentrations in raw wastewater from the small WWTP; WW = wastewater; SW = surface water.) (For interpretation of reference to color in this figure legend, the reader is referred to the web version of this article.)

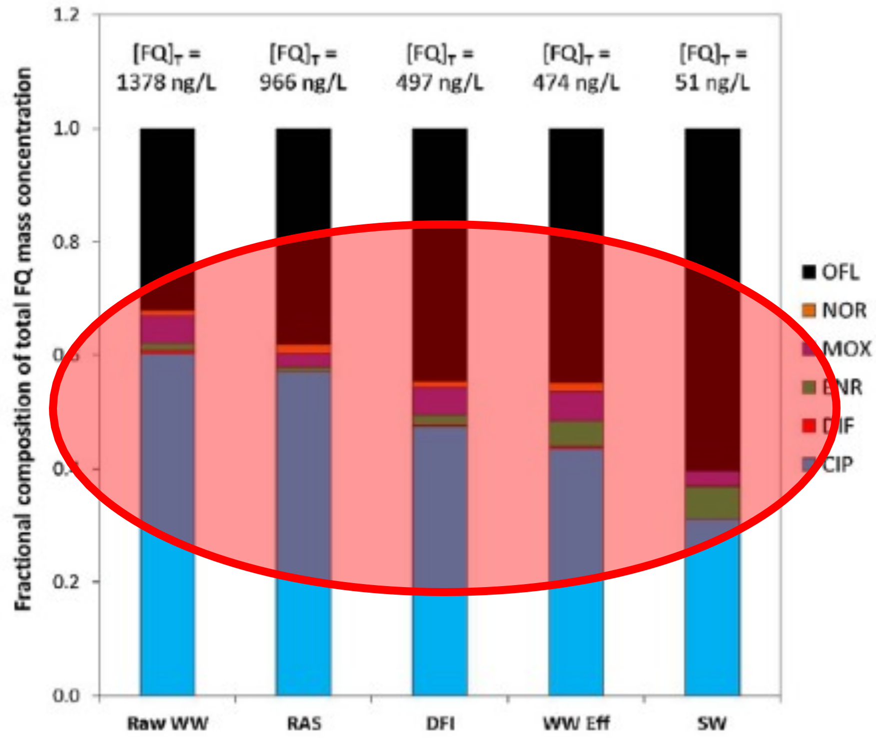
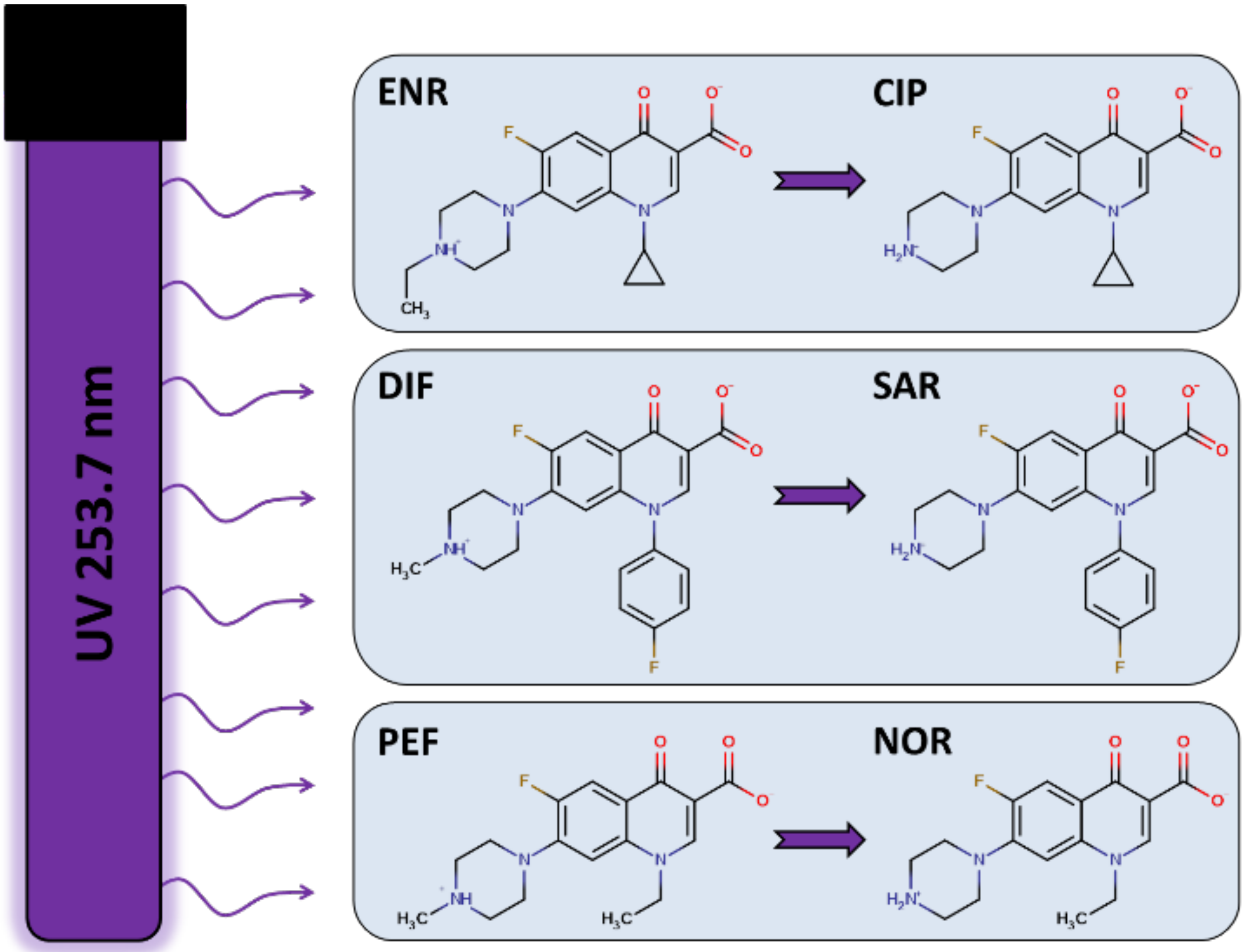


Fig. 4. Normalized column plot showing the relative fraction of each FQ present in different wastewater compartments. (Aggregate concentrations from sampling campaign were used to find the fractional composition; the averaged total mass concentration of FQs is indicated above each column.)

[He *et al.*, 2015]

Some of our observed AB-to-AB transformations



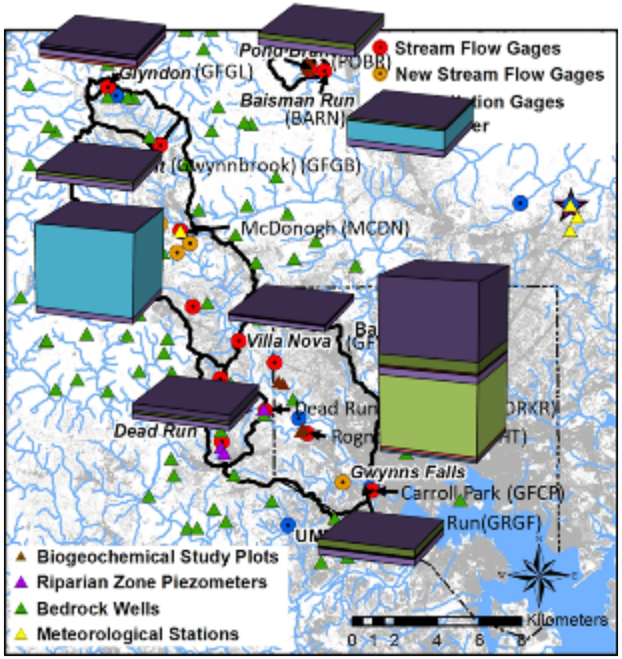
Conclusions

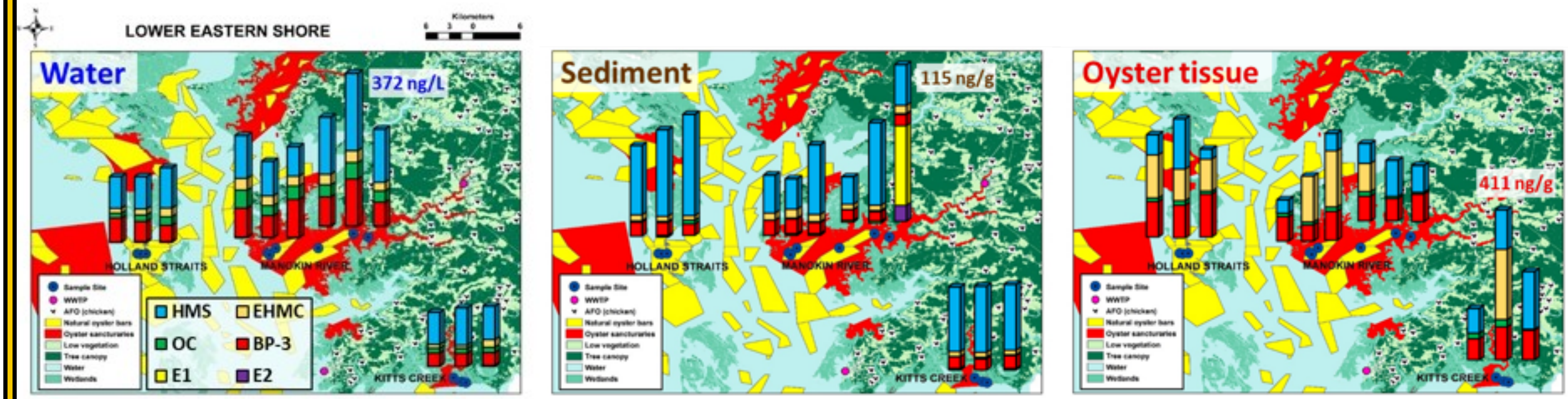
Concluding thoughts

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

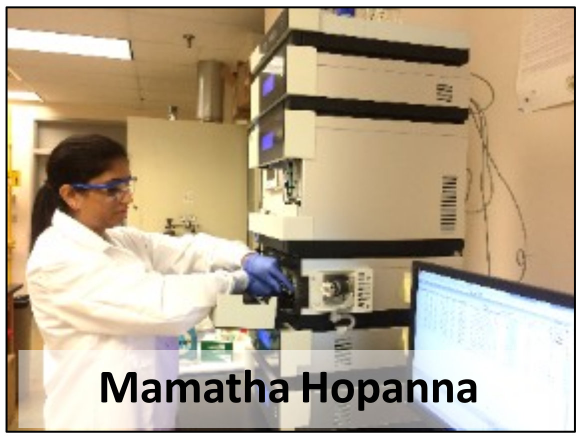
2. CECs are widely present in Chesapeake Bay water, sediment, and oysters and more monitoring studies are required to better understand spatiotemporal trends

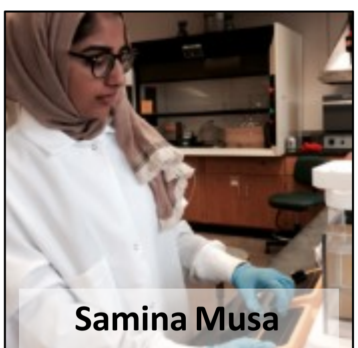
3. As CECs were specifically designed to cause biological response, coupled chemical-response studies should be conducted to investigate unexpected toxicity

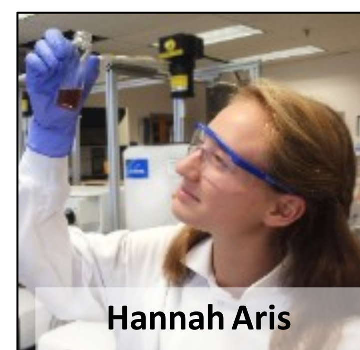




My great team







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Thanks for your attention

Any questions?

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