Expanding environmental monitoring campaigns: Contaminants of emerging concern are also present in "unimpacted" watersheds

Ke He, Lee Blaney

Department of Chemical, Biochemical and Environmental Engineering
University of Maryland Baltimore County

2017 National Environmental Monitoring Conference
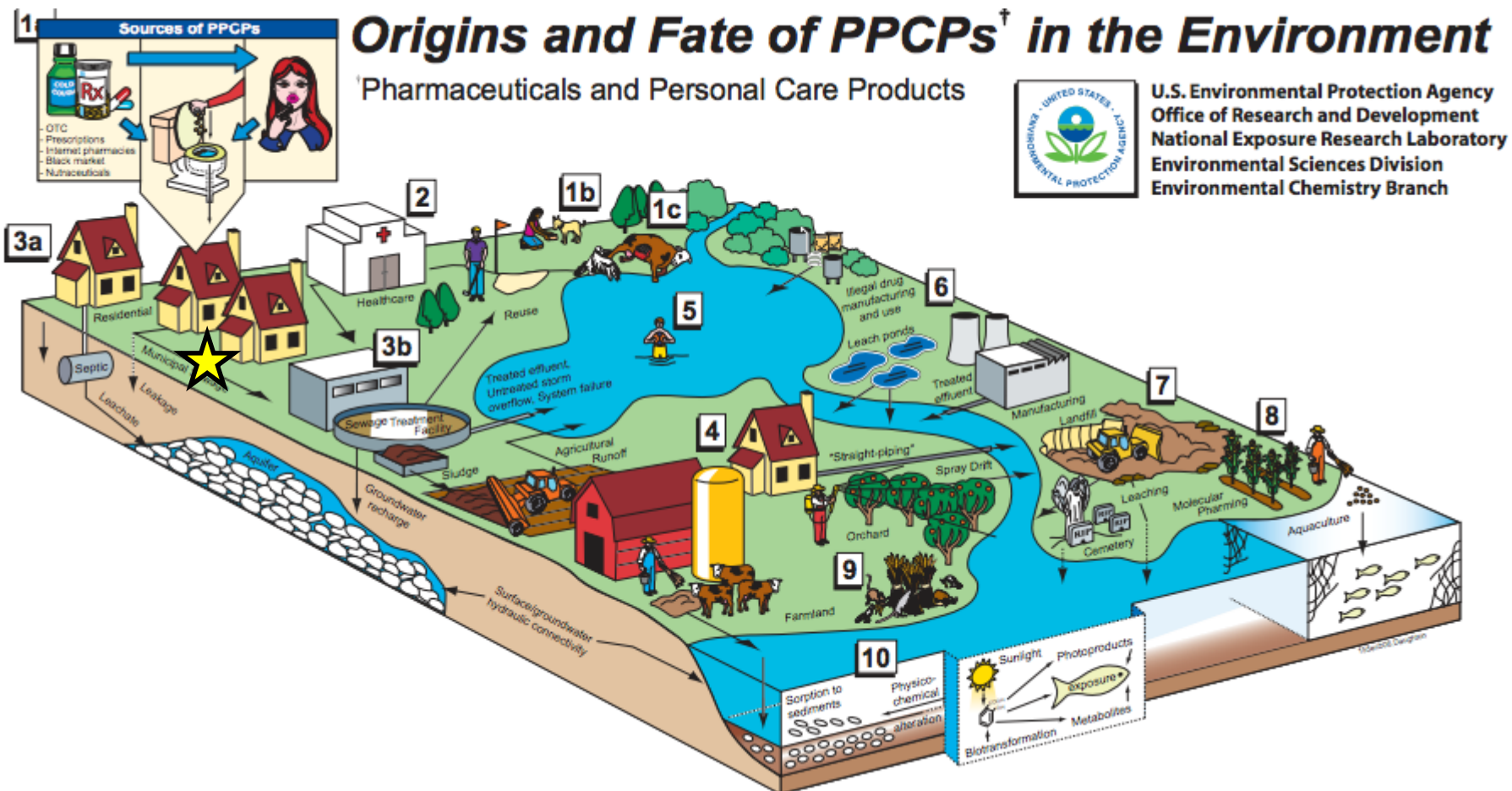*August 7, 2017 (Washington, DC)*

NAE GC – Restore and improve urban infrastructure

Compromised urban wastewater infrastructure highlights the need to consider the fate of contaminants upstream of WWTPs

ENVIRONMENT BY FERN SHEN 12:00 PM APR 25, 2016 (6)

Chinquapin Run sewage leak went 23 days before city reported it

Upstream was a sewage leak that one city agency had known about for days. Downstream was a fishing derby for kids organized by another agency.

Sources of CECs – revisiting assumptions

Origins and Fate of PPCPs† in the Environment
†Pharmaceuticals and Personal Care Products

U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Environmental Sciences Division
Environmental Chemistry Branch

Wastewater leaks are common occurrences

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...

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.

Roads Reopen After Sewage Spill In Frederick
Frederick County officials say roads have reopened following a raw sewage spill at the city's waste water treatment plant.

Sewage Spill Closes C&O Canal Section
A sewage spill has closed part of the Chesapeake and Ohio Canal in Washington County.

More Sewage Spills Into Patapsco River
More sewage has spilled into the Patapsco River, which saw 100 million gallons of raw sewage spill after Hurricane Irene.

Baltimore City Tries To Stop Sewage Spill
More than 10 thousand gallons of raw sewage have poured into Herring Run and workers are still trying to stop the spill.

"We get what we measure"

Sampling campaigns for CECs focus on expected sites

- 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.

My objectives for today

1. To examine the ability of **fluorescence excitation emission matrices** (EEMs) to highlight water quality disturbances in urban streams

2. To quantify concentrations of **contaminants of emerging concern** (CECs) in an unimpacted, urban watershed

We propose that these parameters can be used as forensics tools to not only locate sewer leaks, but also examine the occurrence, fate, transport, and impacts of CECs in urban streams.

Study site – Gwynns Falls watershed (Baltimore, MD)

The 2004 water quality management plan states, "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".
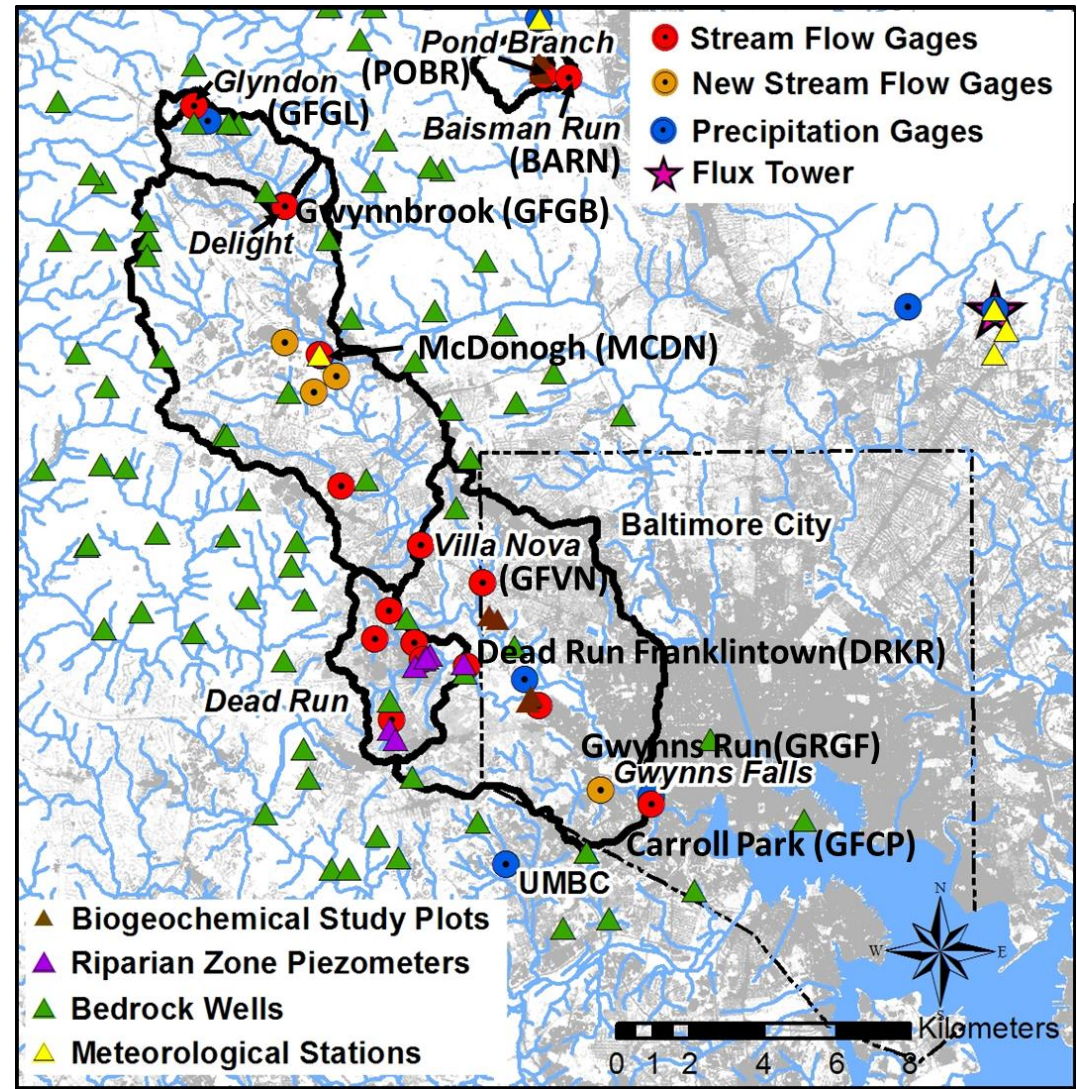
Source: Baltimore Ecosystem Study

Part 1:

Excitation emission matrices as screening tools for water quality changes in urban streams

EEMs act as a solution fingerprint (DOM)

Hypothesis: Sewer leaks introduce wastewater DOM to urban streams, and that DOM can be identified by its fluorescence signature
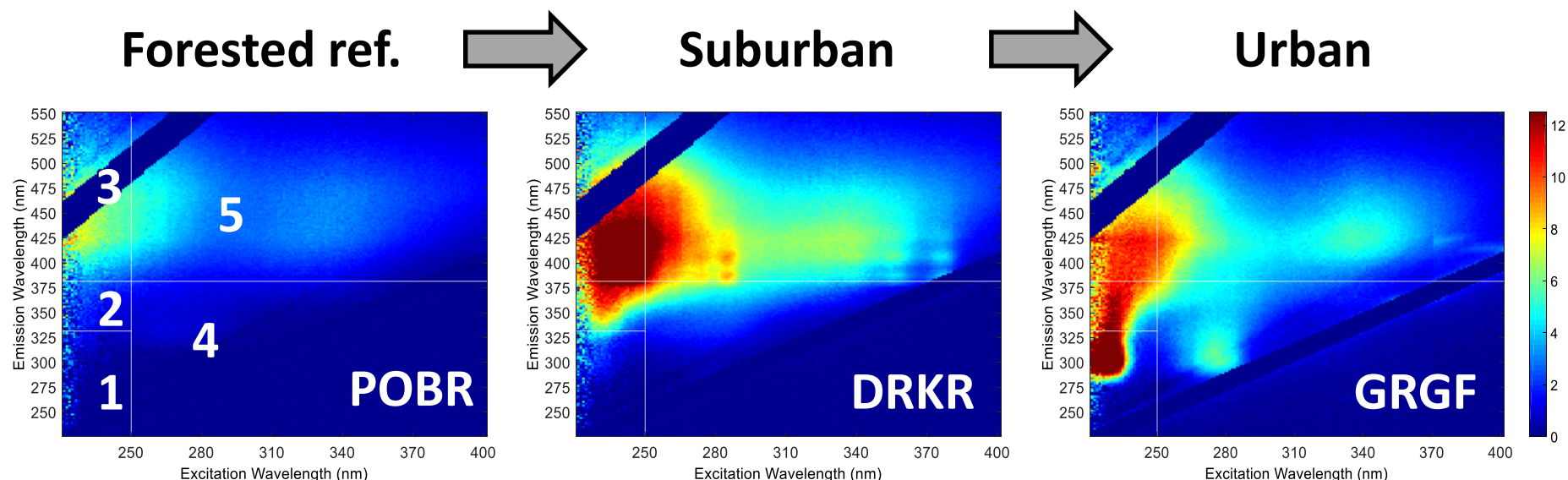
Region 1: Tyrosine-like aromatic protein

Region 2: Tryptophan-like aromatic protein

Region 3: Fulvic acid-like

Region 4: Soluble microbial product-like

Region 5: Humic acid-like

(Chen *et al.*, 2003)

Fluorescence signatures correlated to land use

The rural-to-urban flow gradient was captured by plotting a fluorescence index corresponding to fulvic acid-like molecules against an index for soluble microbial products
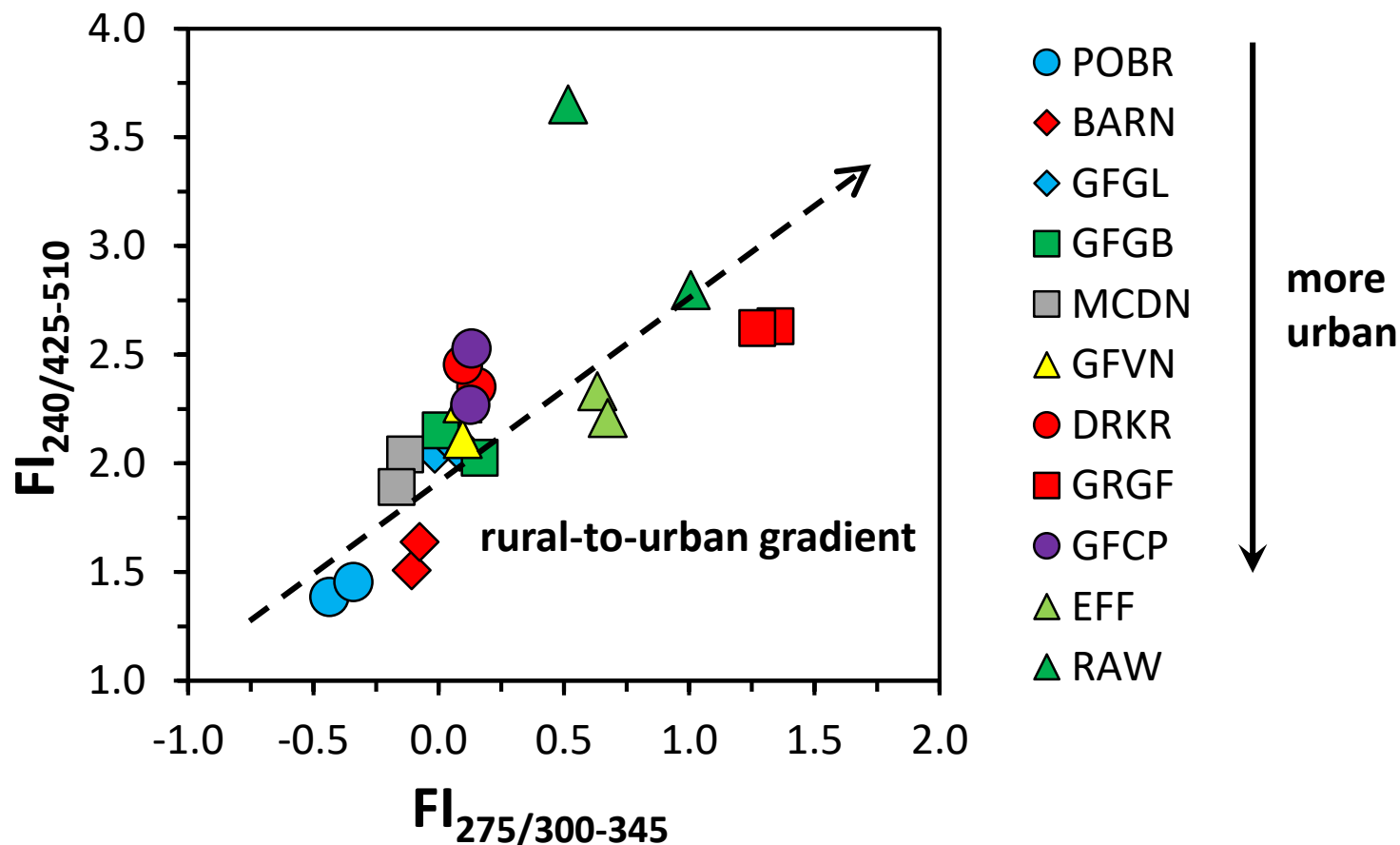
EEMs showed local disturbances in water quality

5750–6050 m upstream of DRKR
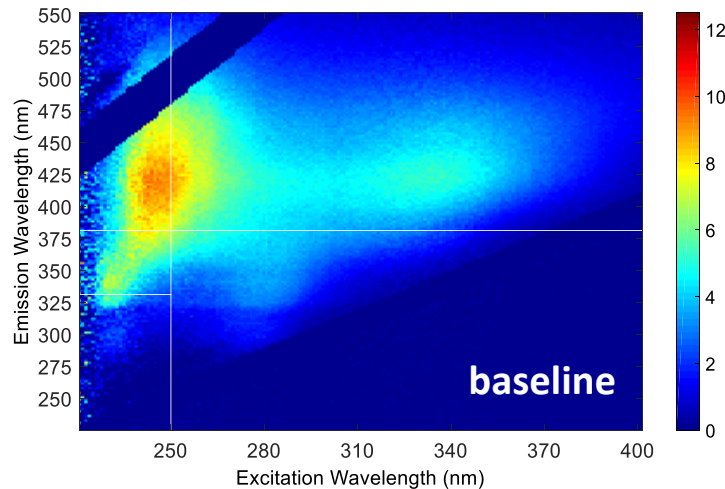
5100-5600 m upstream of DRKR
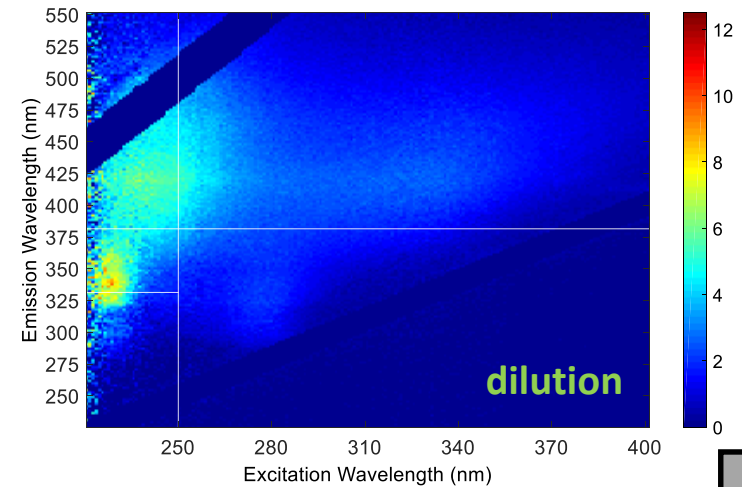
2100-3300 m upstream of DRKR
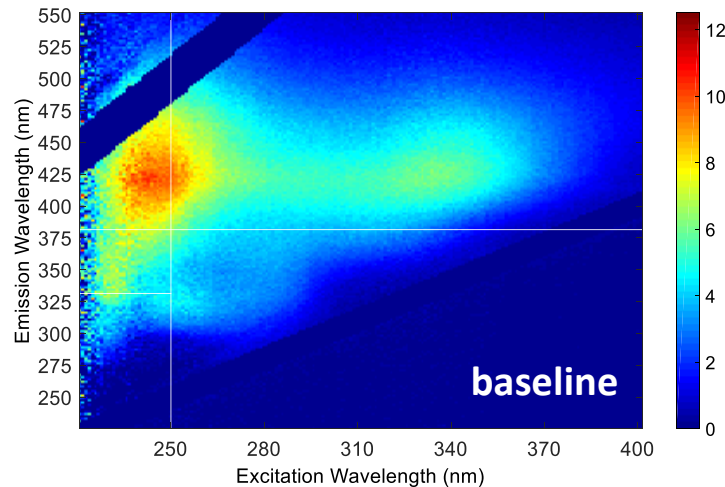
4550-5000 m upstream of DRKR
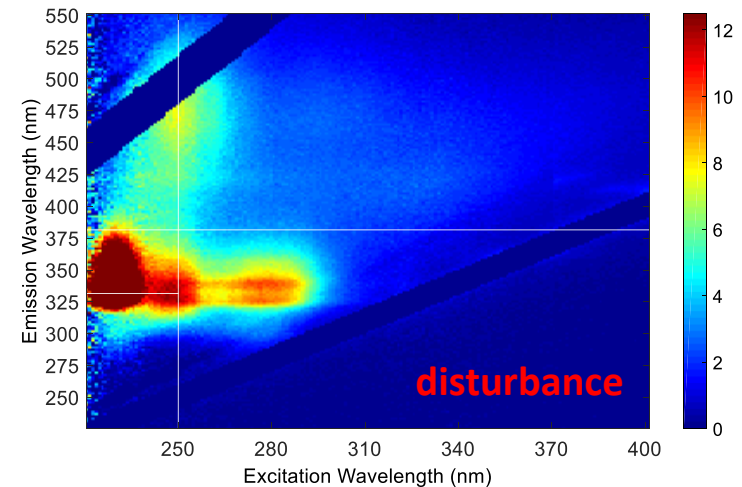
Regional analysis indicated a location of interest
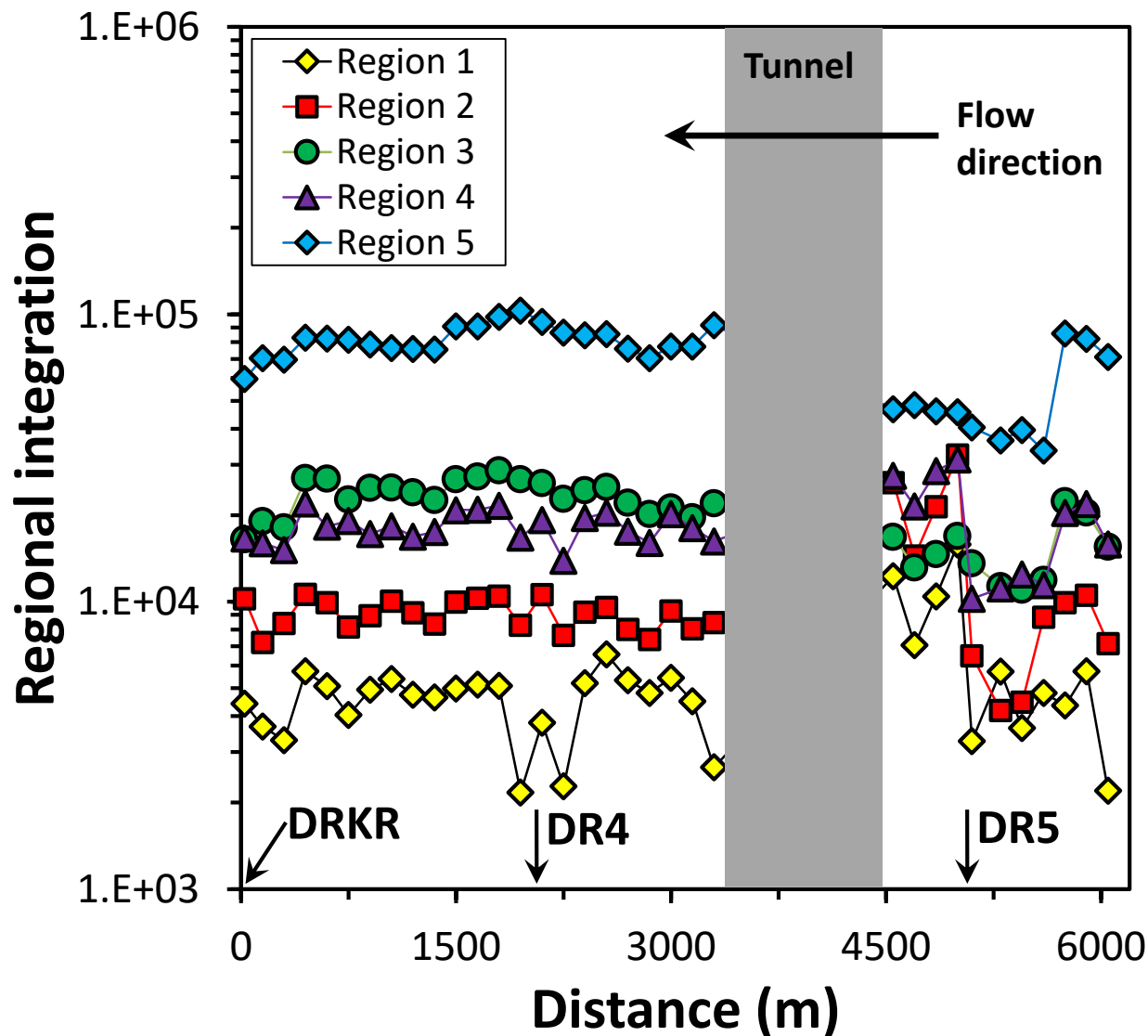
Part 2:

CECs in unimpacted urban watersheds highlight impacts of wastewater leaks

Following up on location of interest in Dead Run

Hypothesis: CECs are present in unimpacted urban streams and can be used in tandem with EEMs to identify sources of contamination

Our earlier work showed the presence of a wide variety of fluoroquinolones in Gwynns Falls

[He *et al.*, 2015]
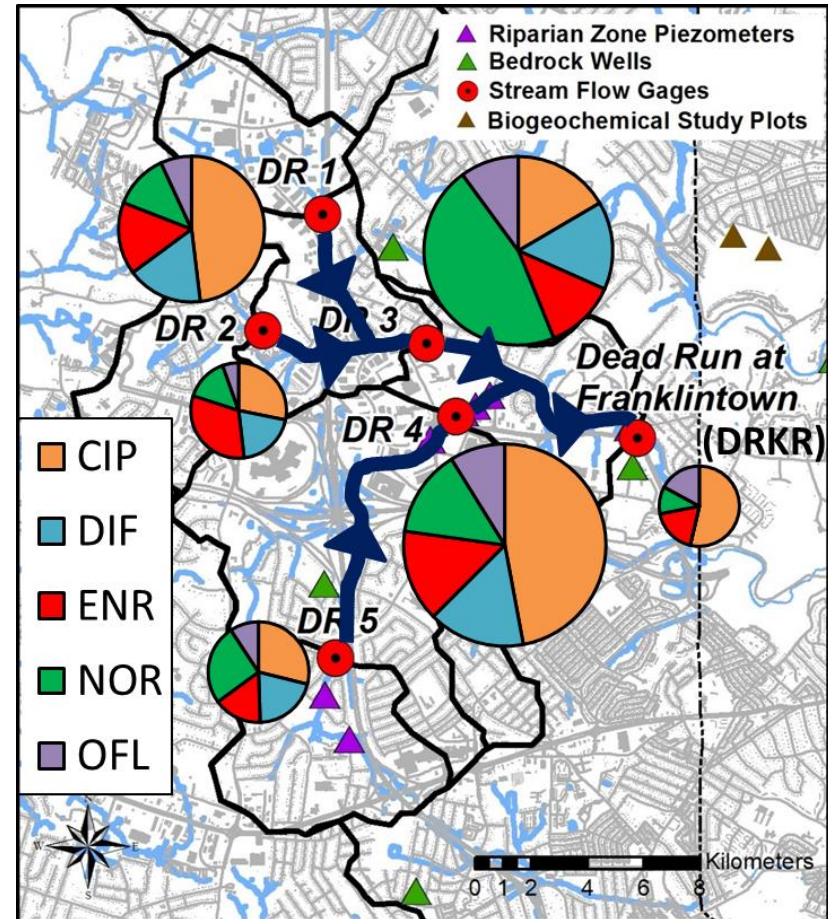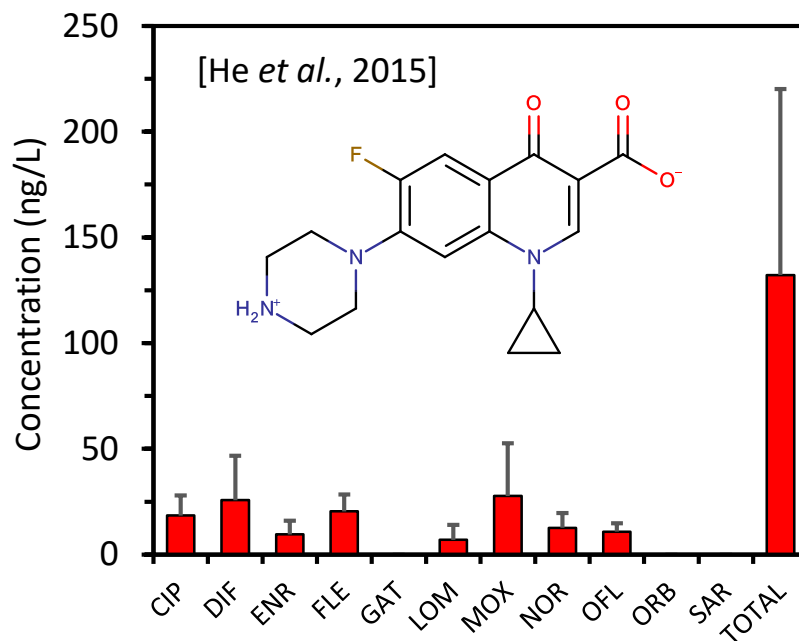
* Average of eight sampling events

We conducted two 10-week sampling campaigns in 2016

Collected samples from 13 sites in the Gwynns Falls watershed for analysis of 17 fluoroquinolones, 13 sulfonamides, 8 tetracyclines, 5 macrolides, 3 estrogens, and 5 UV-filters.
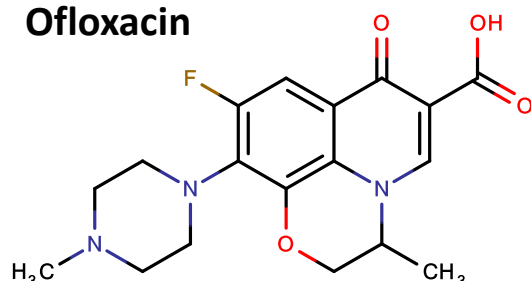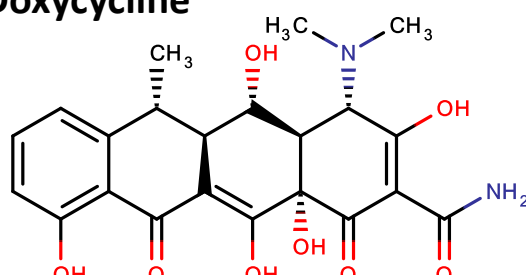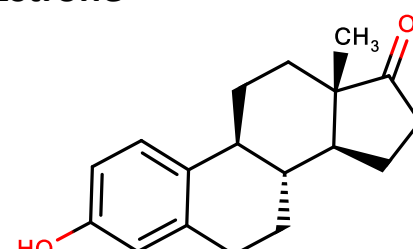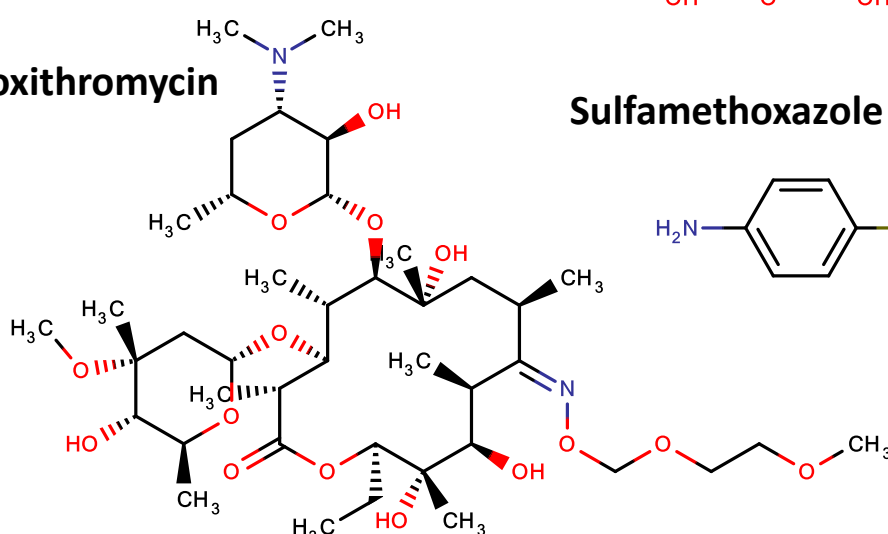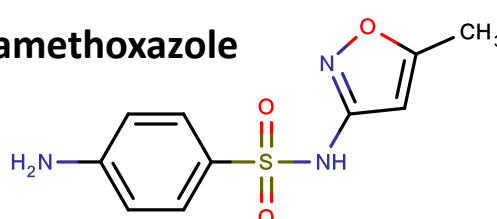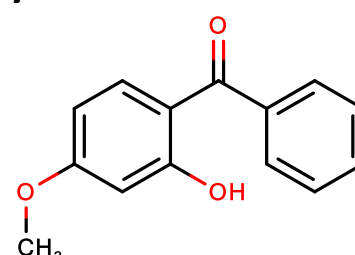
All analytes were measured using SPE with LC-MS/MS

For the sake of brevity, full analytical methodologies are not included here…
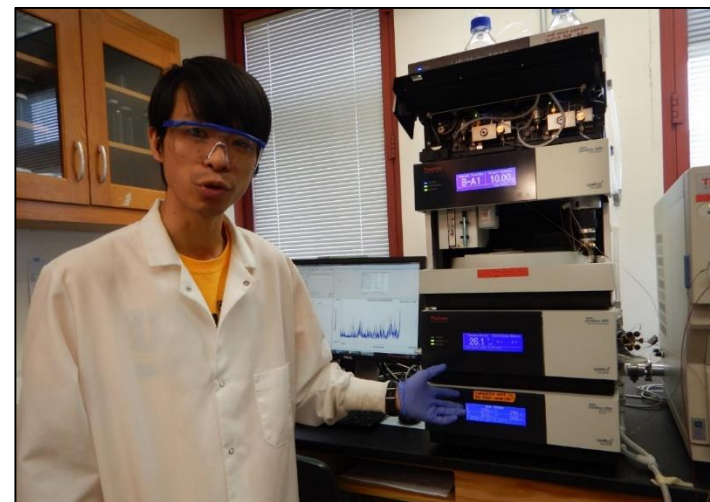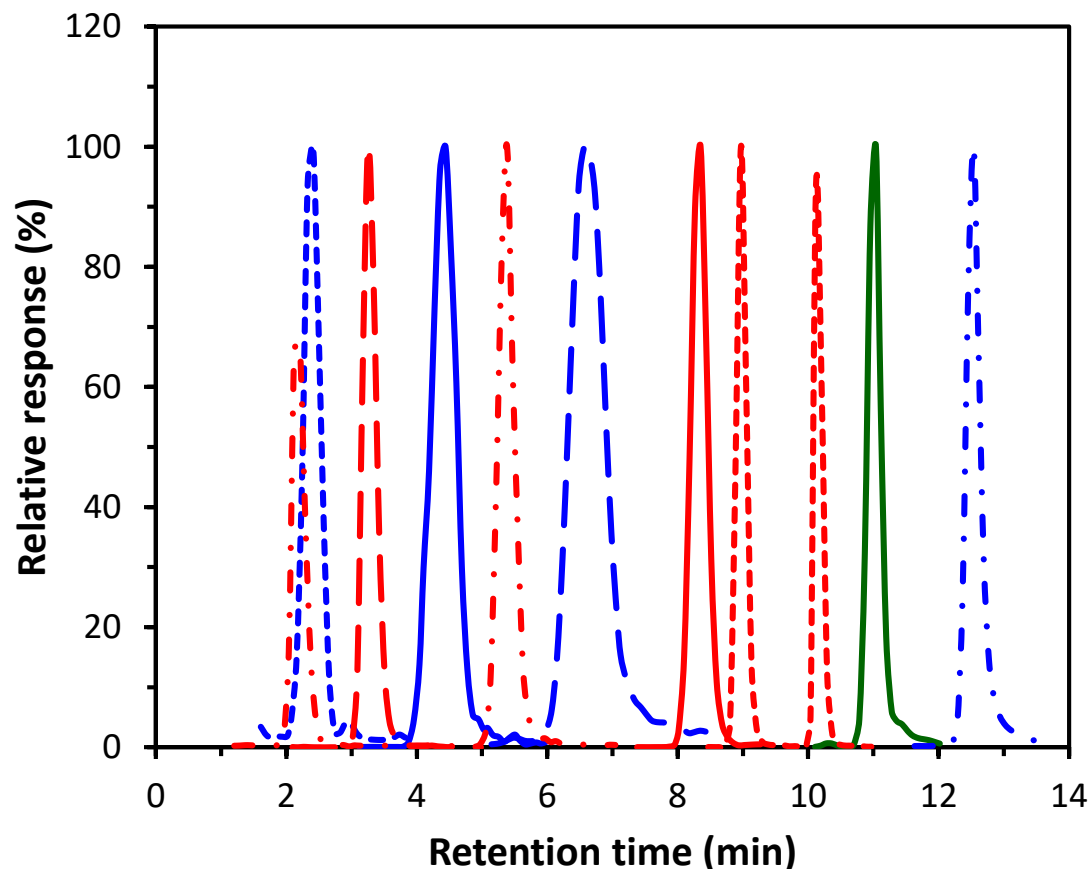
A wide variety of antibiotics were detected

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
Meclocycline *	42.2	17,700
Methacycline	2.5	215

ERY
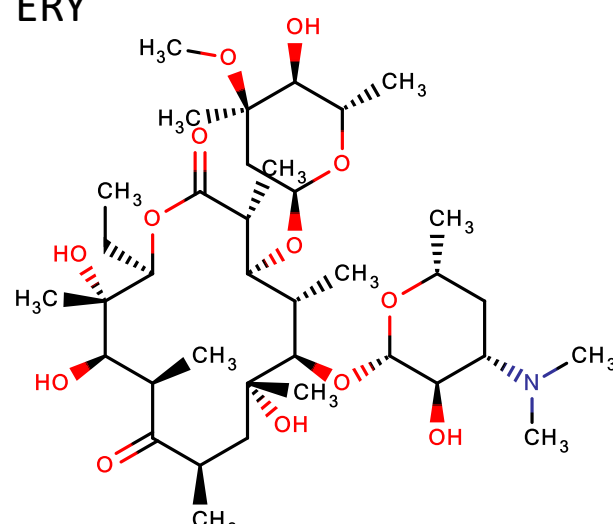
SMX
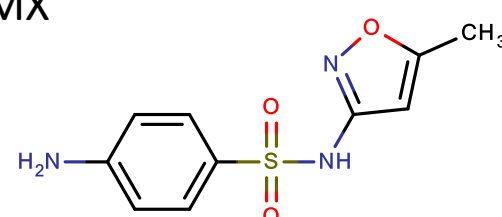
Spatiotemporal trends in antibiotic concentrations
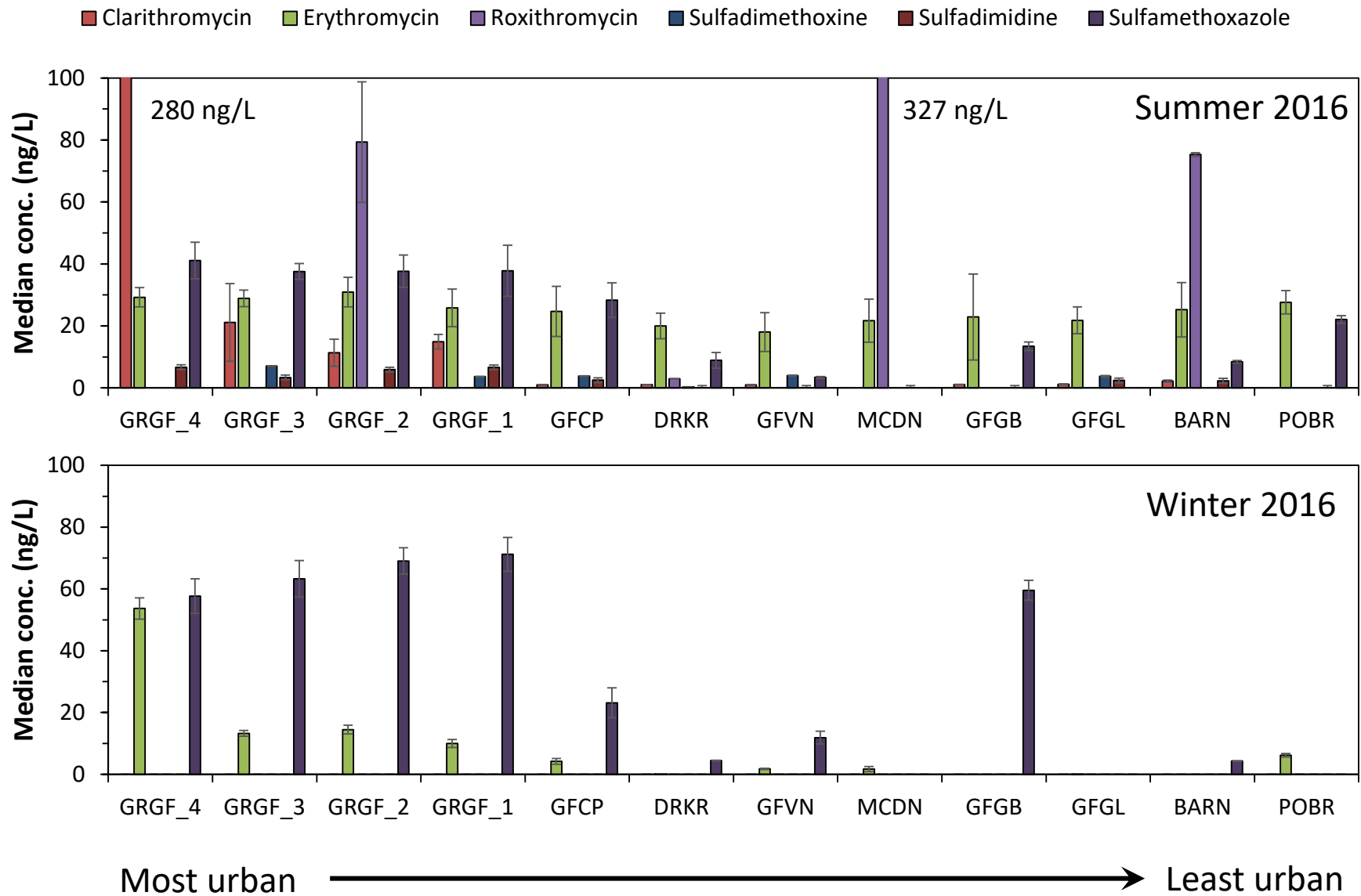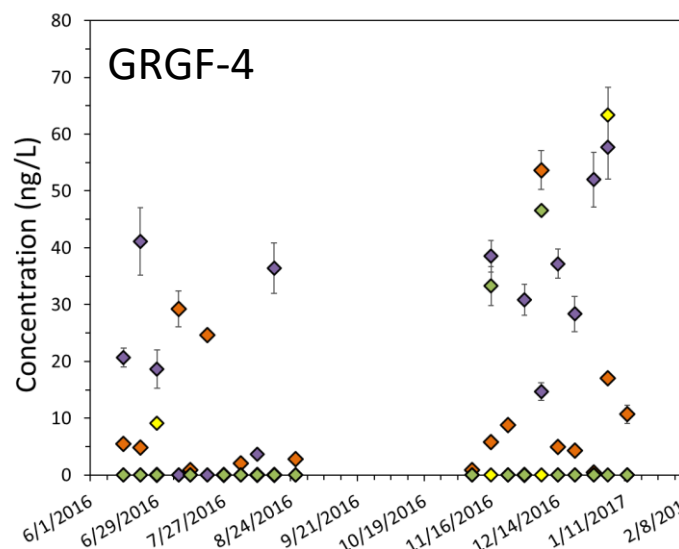
Hydrological profiles in Gwynns Falls watershed
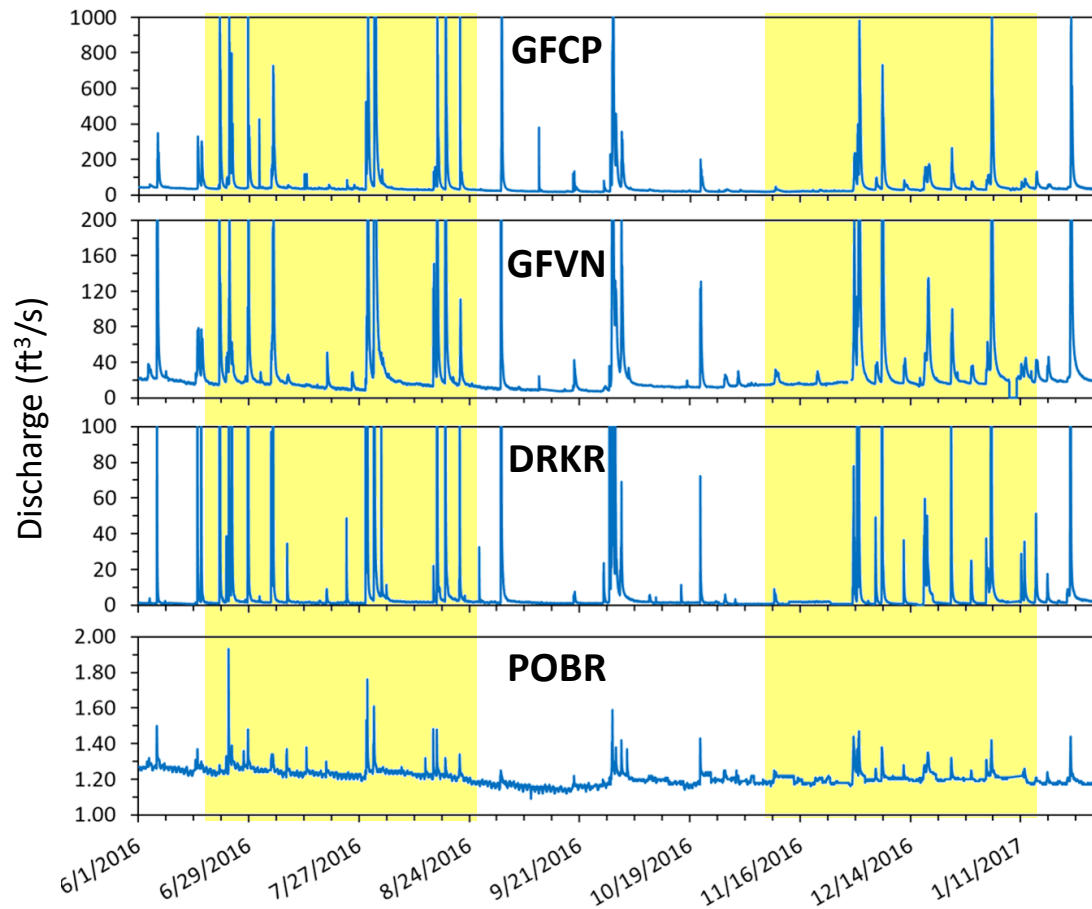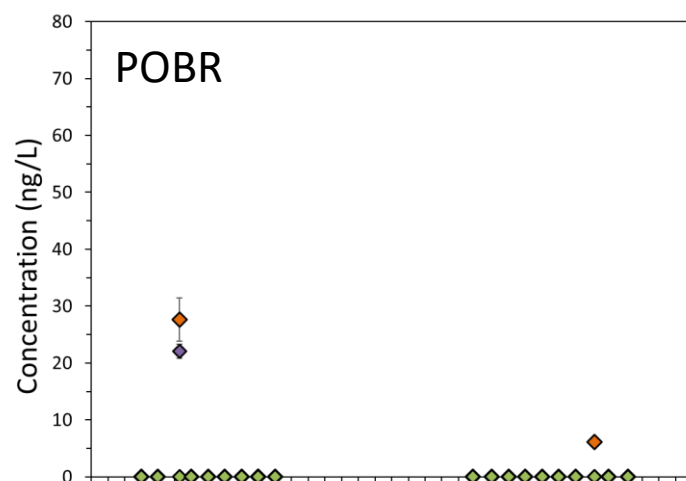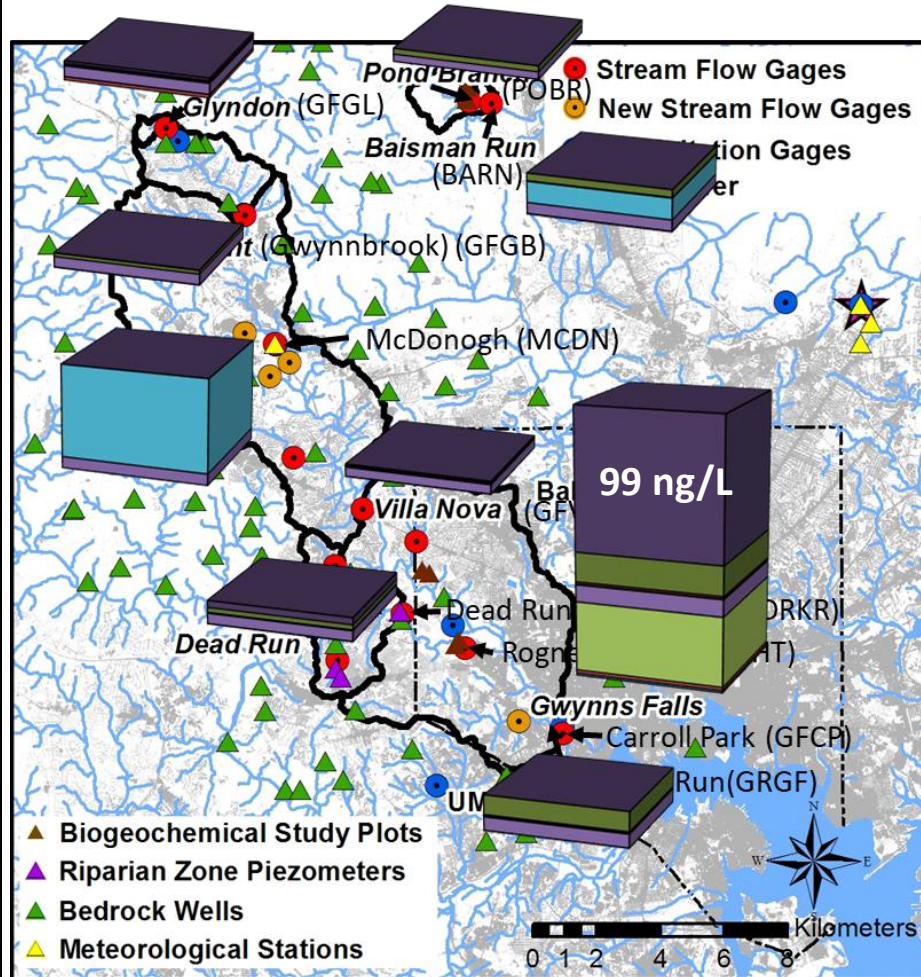

Source: USGS NWIS
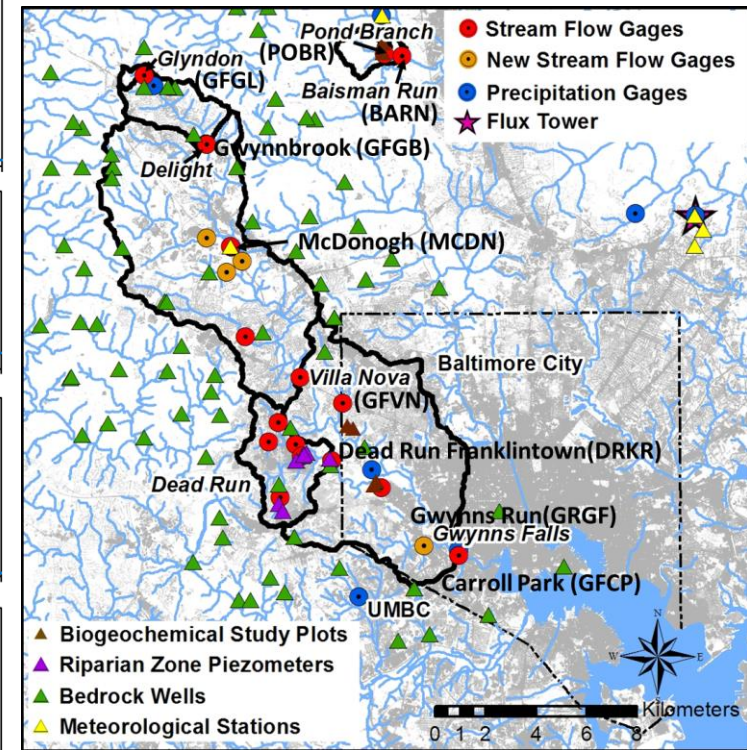
Antibiotic time series for rural (low) → urban (high) sites
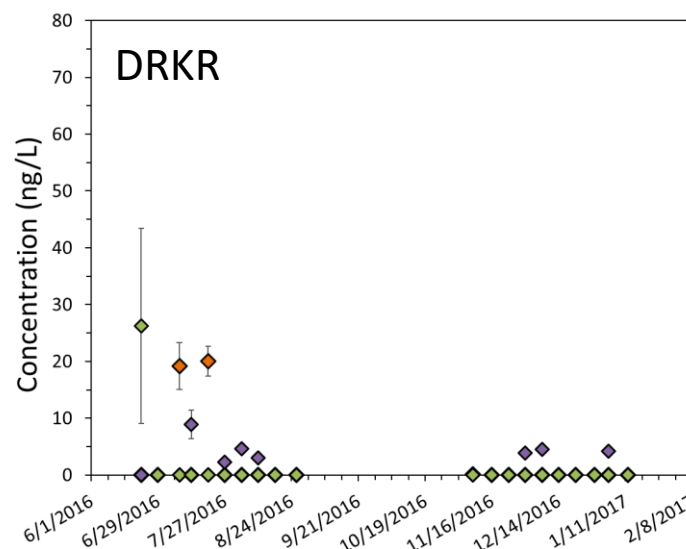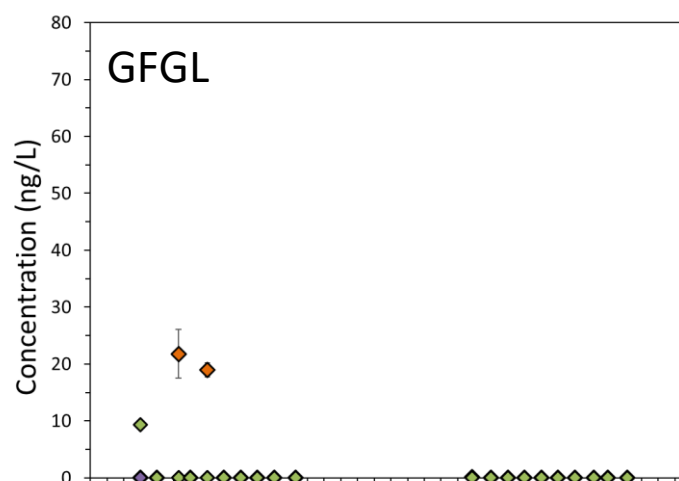
Mapping antibiotics in Gwynns Falls watershed (mean)
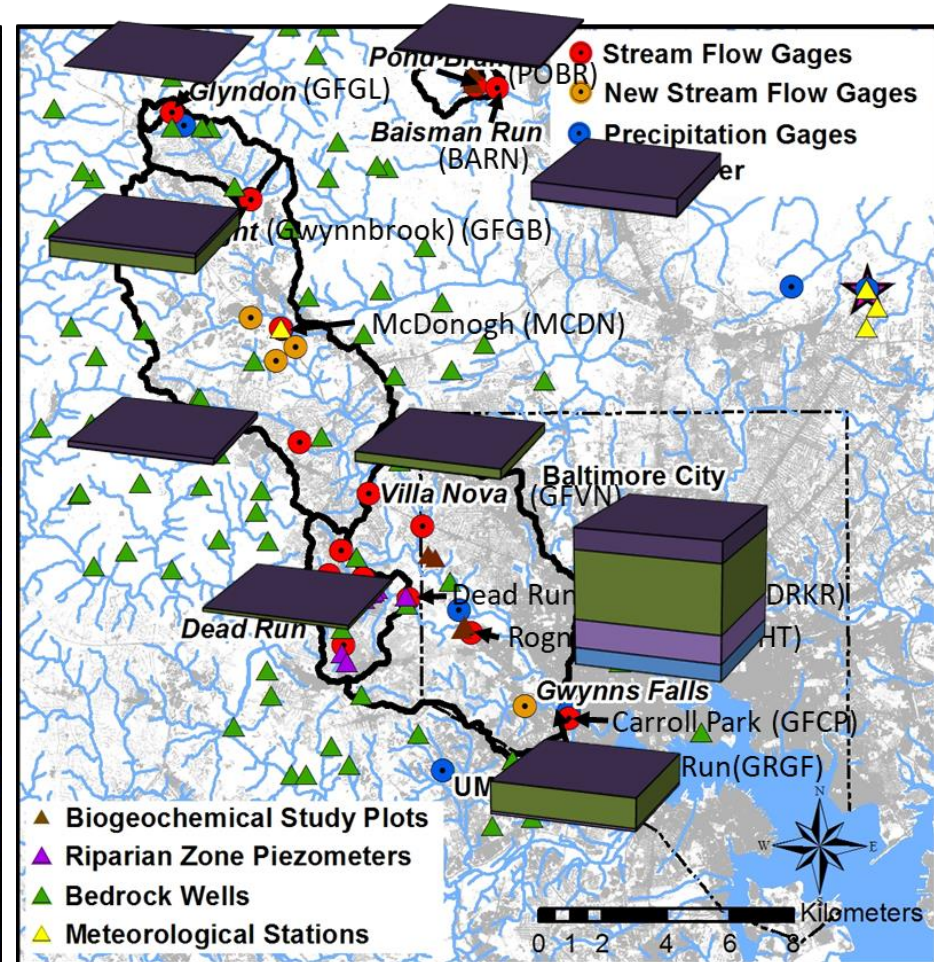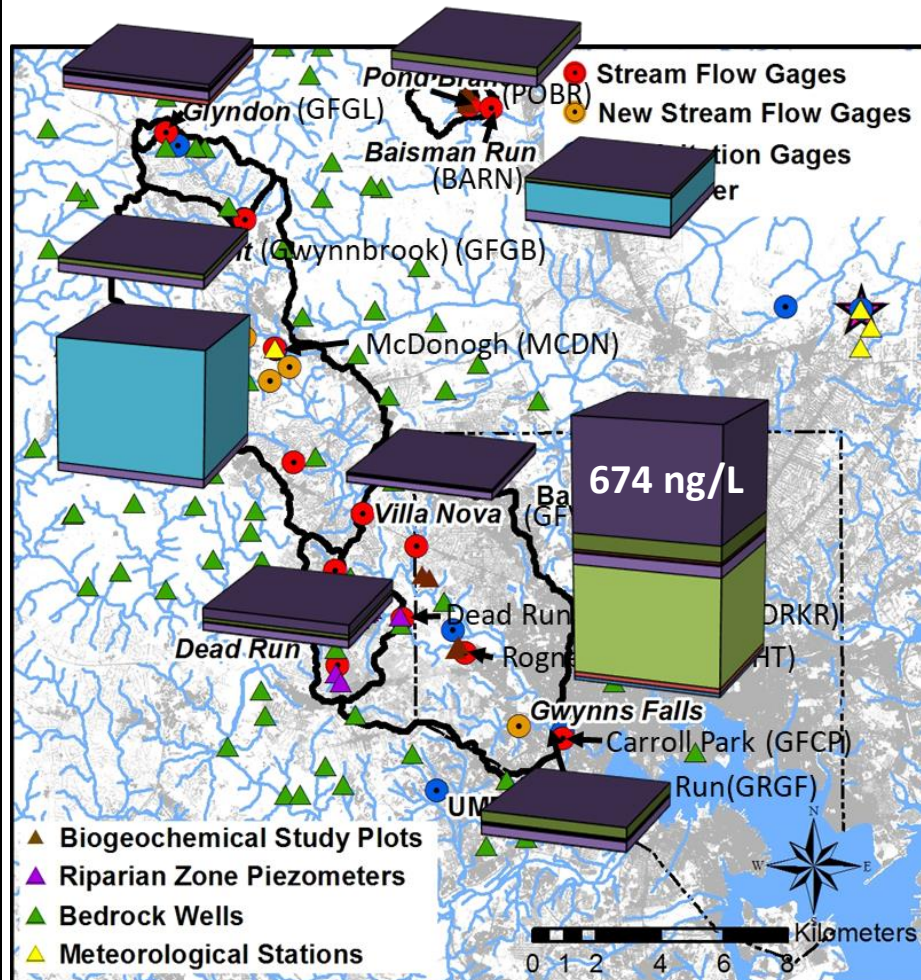
Summer mean

Winter mean

99 ng/L

Legend:
- ■ Doxycycline
- ■ Sulfamethoxazole
- ■ Sulfadimidine
- ■ Sulfadimethoxine
- ■ Tylosin
- ■ Roxithromycin
- ■ Erythromycin
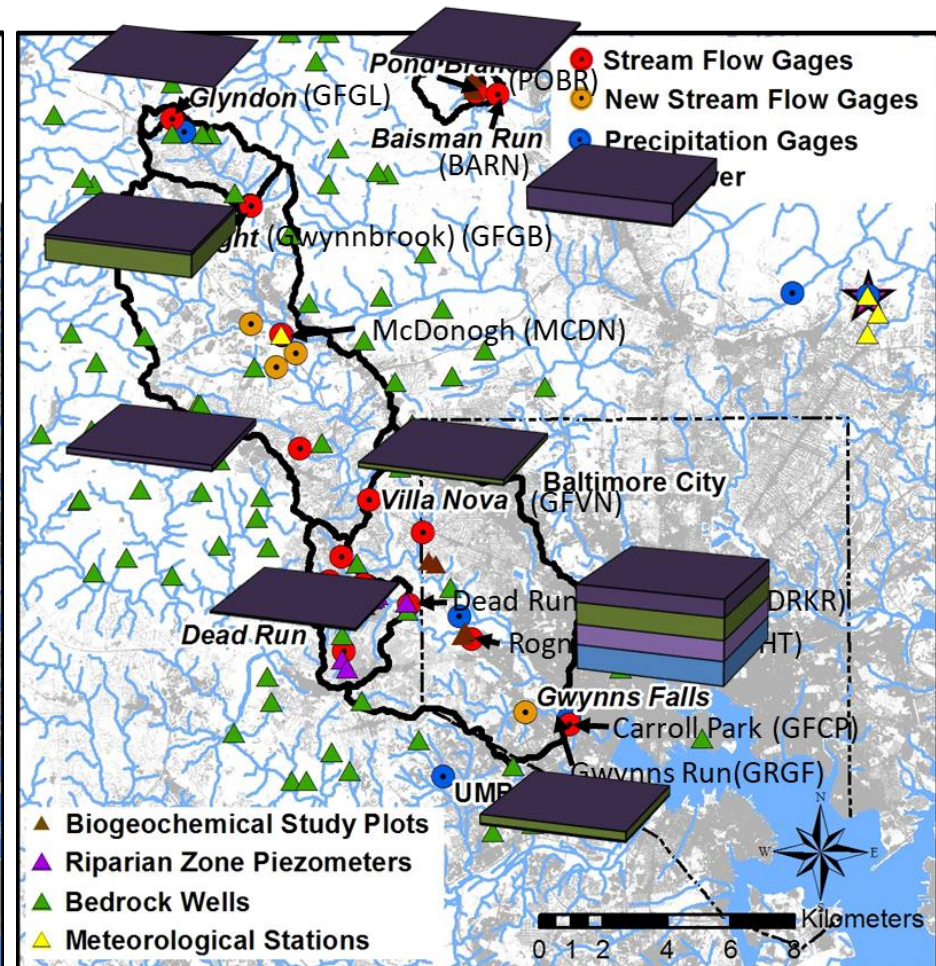- ■ Clarithromycin
- ■ Azithromycin
- ■ Ofloxacin

Map legend items:
- ▲ Biogeochemical Study Plots
- ▲ Riparian Zone Piezometers
- ▲ Bedrock Wells
- ▲ Meteorological Stations
- ● Stream Flow Gages
- ◉ New Stream Flow Gages
- ● Precipitation Gages

Mapping antibiotics in Gwynns Falls watershed (max)

Summer maximum — **Winter maximum**

674 ng/L

Legend:
- Stream Flow Gages
- New Stream Flow Gages
- Precipitation Gages
- Biogeochemical Study Plots
- Riparian Zone Piezometers
- Bedrock Wells
- Meteorological Stations

Antibiotics: Doxycycline, Sulfamethoxazole, Sulfadimidine, Sulfadimethoxine, Tylosin, Roxithromycin, Erythromycin, Clarithromycin, Azithromycin, Ofloxacin
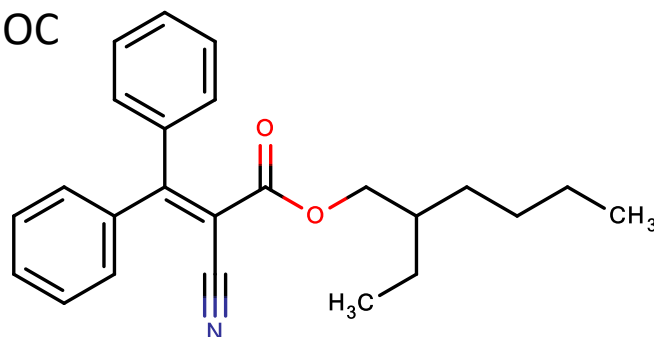
UV-filters are widely present in the Gwynns Falls

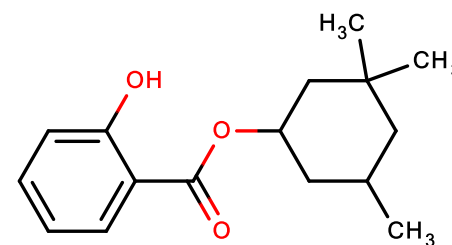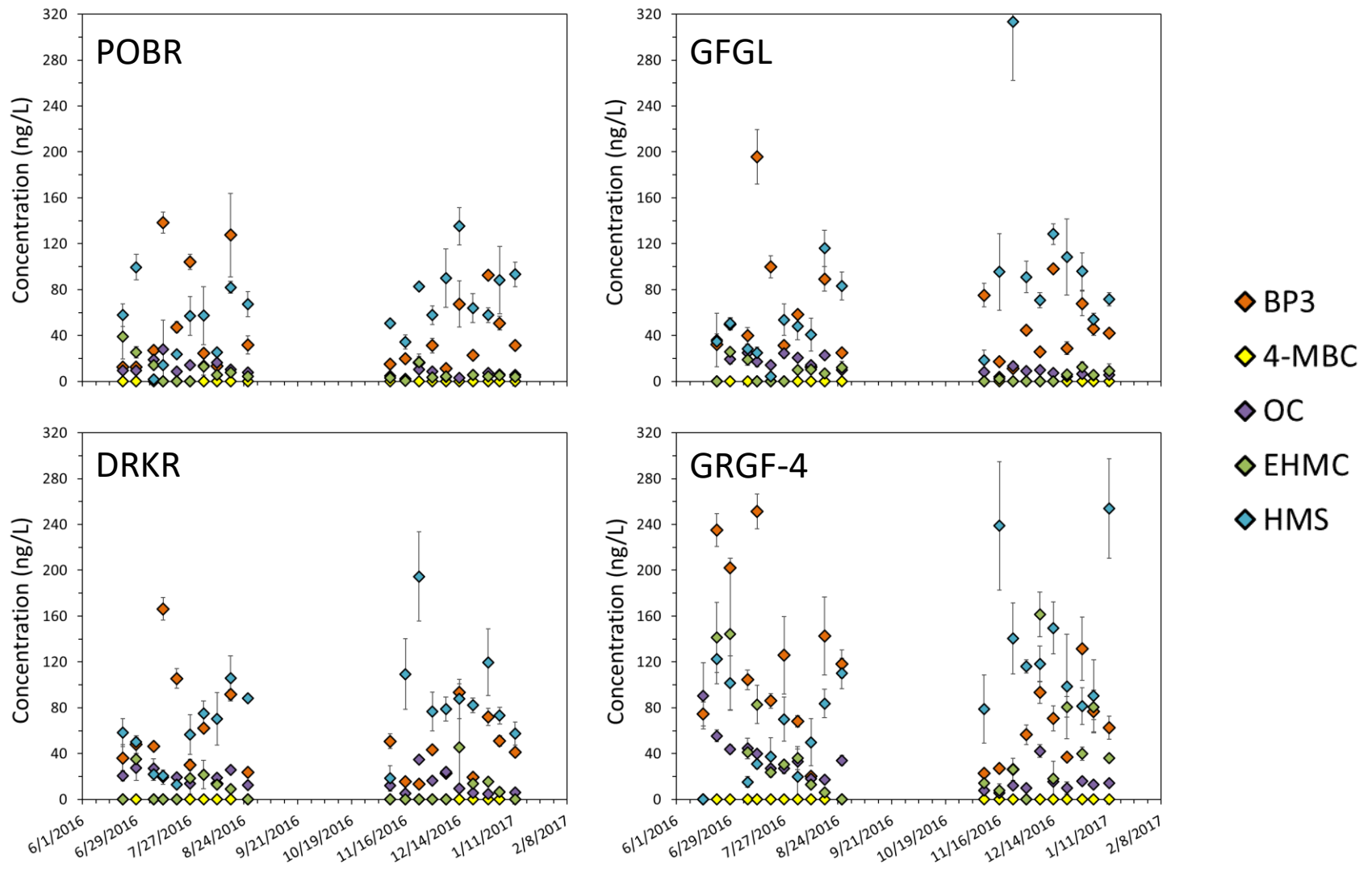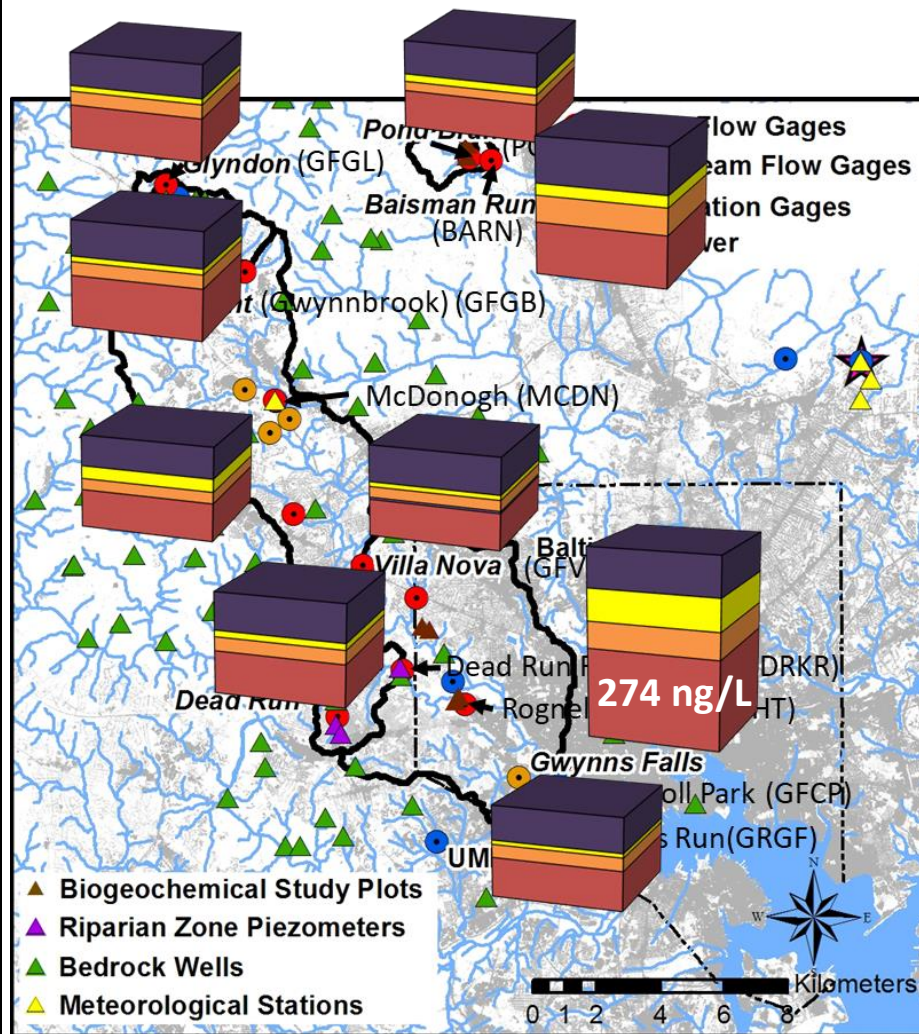| Compound	Detection frequency (%)	Maximum concentration (ng/L)
17α-ethinylestradiol	-	-
Estradiol	-	-
Estrone	41.4	6.4
Oxybenzone	**100**	251
4-Methylbenzylcathinone	1.2	31
Octocrylene	**100**	168
Ethylhexyl methoxycinnamate	68	161
Homosalate	**98**	314

BP3
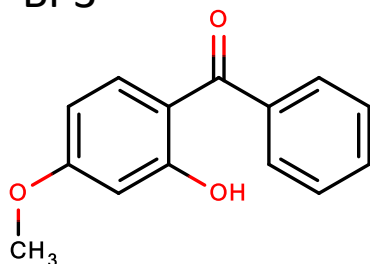
OC

HMS

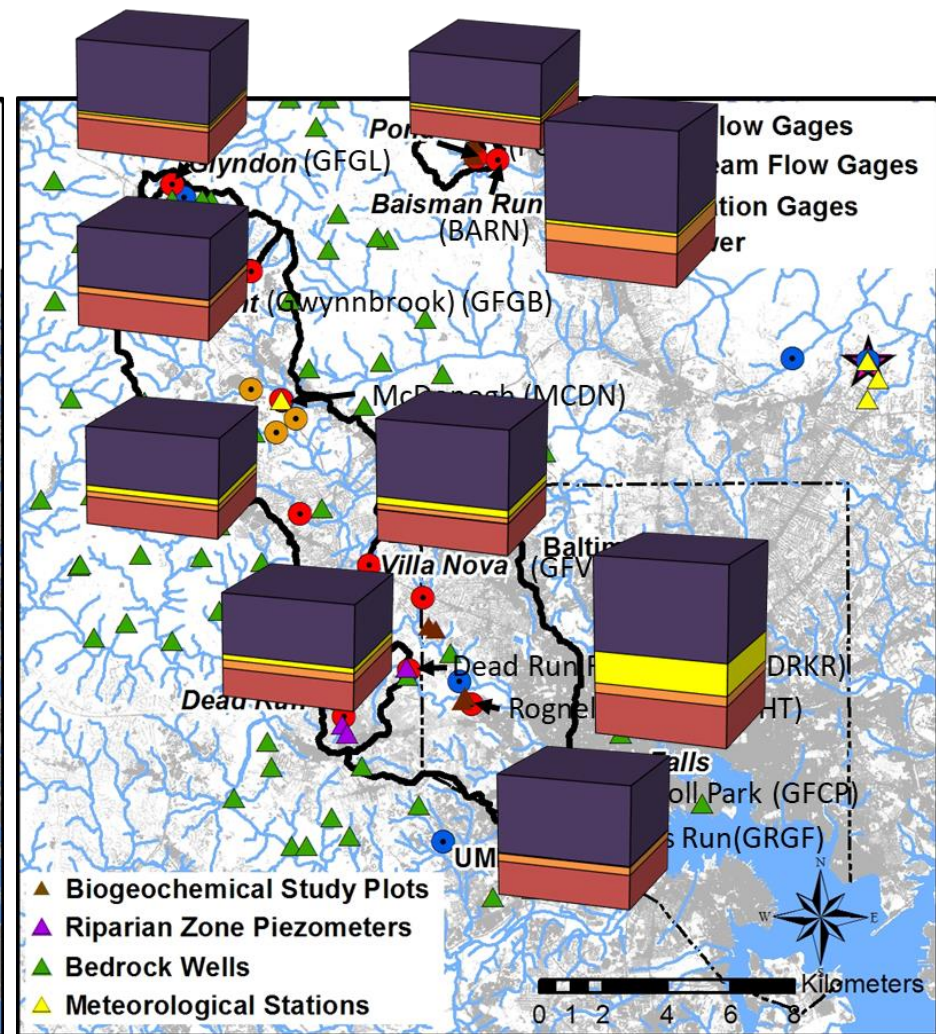# UV-filters ubiquitously present, but urban effect observed

Mapping UV-filters in Gwynns Falls watershed (mean)
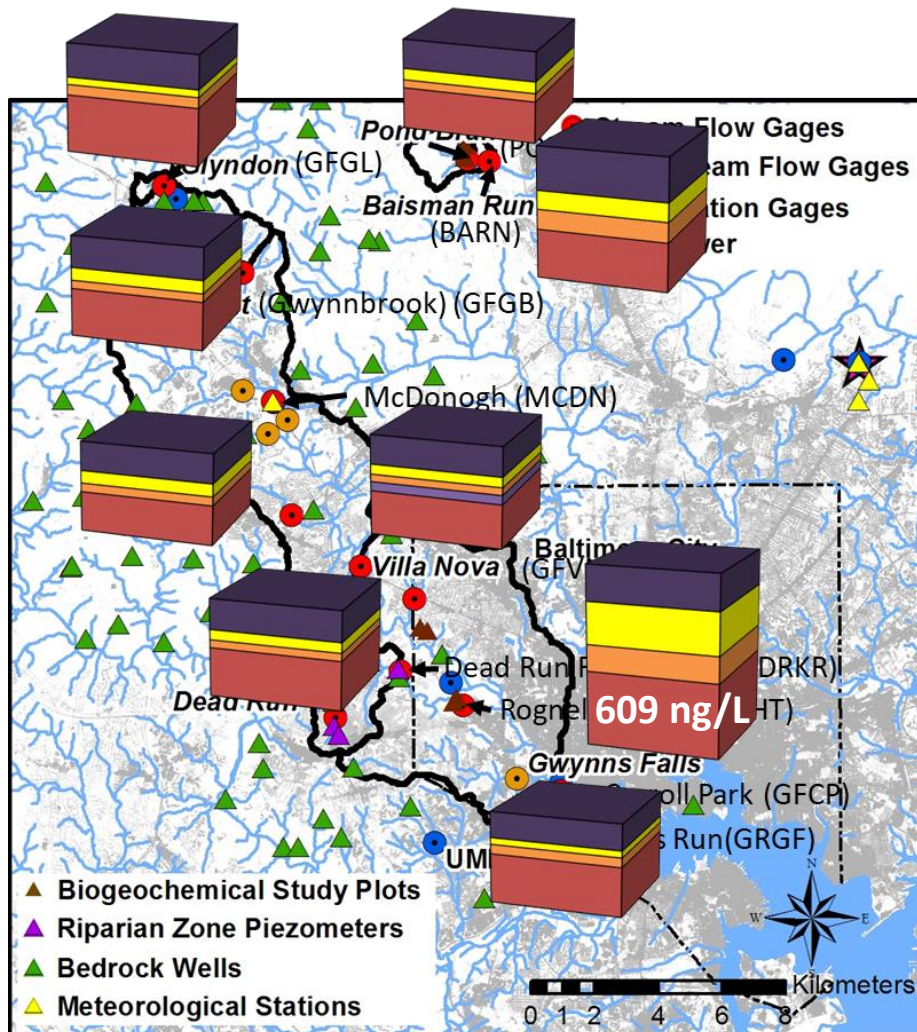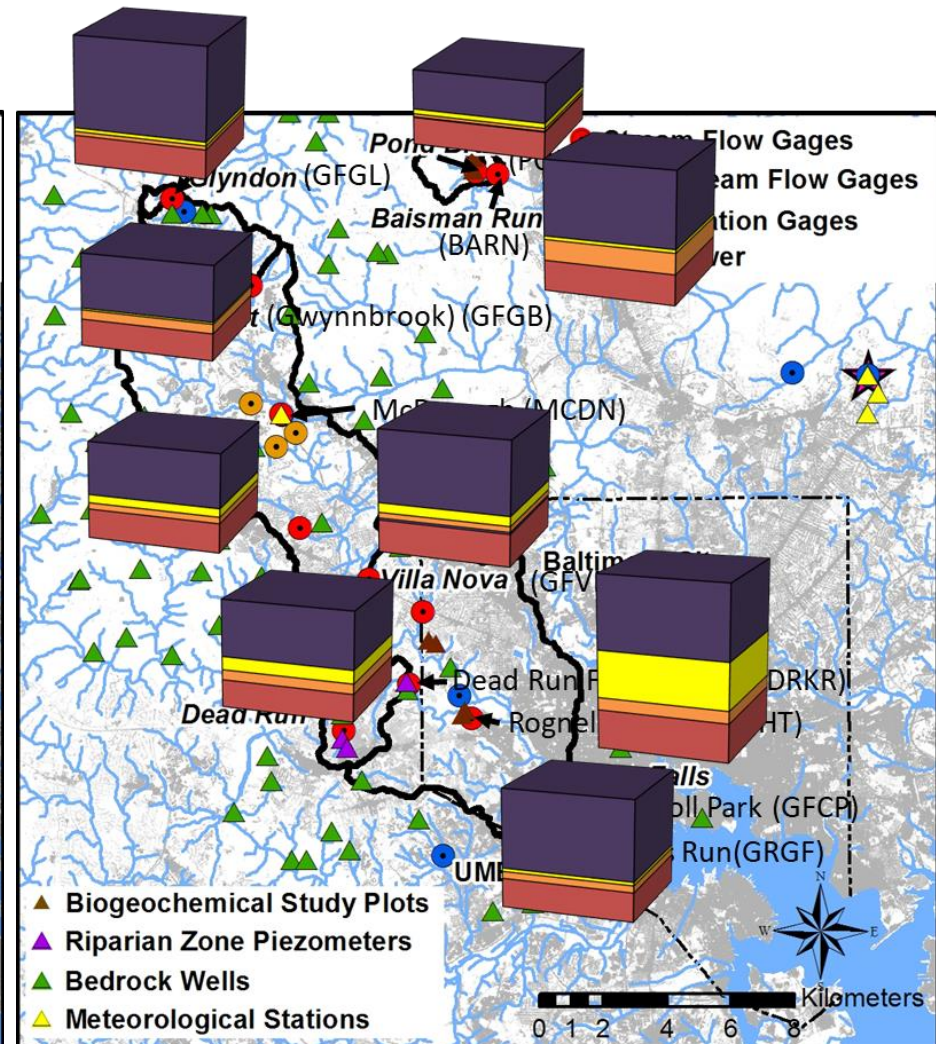
Summer mean

Winter mean

Legend:
- ▲ Biogeochemical Study Plots
- ▲ Riparian Zone Piezometers
- ▲ Bedrock Wells
- ▲ Meteorological Stations

■ HMS ■ EHMC ■ OC ■ 4-MBC ■ BP3

Mapping UV-filters in Gwynns Falls watershed (max)

Summer maximum

Winter maximum

609 ng/L

Legend:
- ▲ Biogeochemical Study Plots
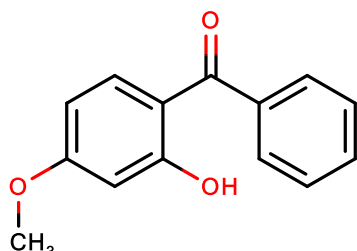- ▲ Riparian Zone Piezometers
- ▲ Bedrock Wells
- ▲ Meteorological Stations
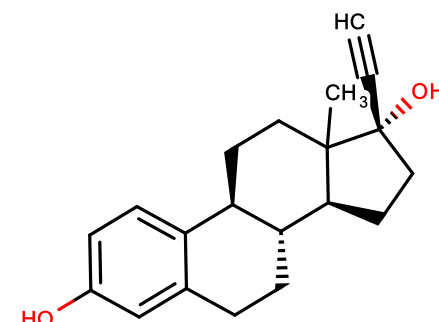
■ HMS ■ EHMC ■ OC ■ 4-MBC ■ BP3

The consistent [UV-filter] suggested a continuous source

BP3: 23.7±0.3 ng/g

EE2: 17.1 ± 1.6 ng/g
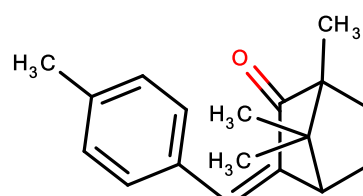
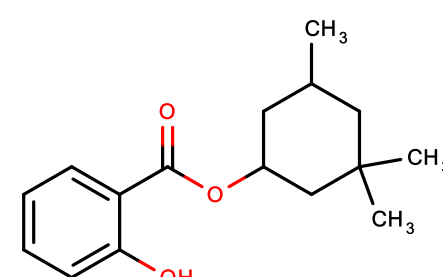**OC: 113±6 ng/g**
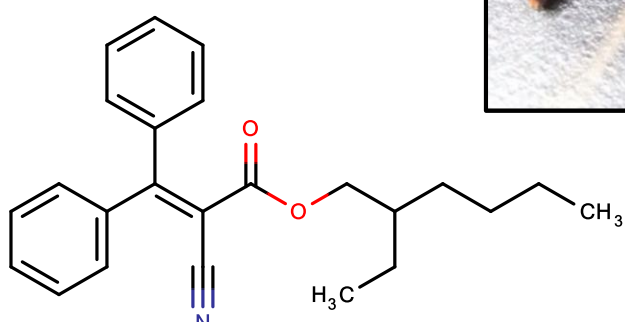
HMS: 260 ± 16 ng/g
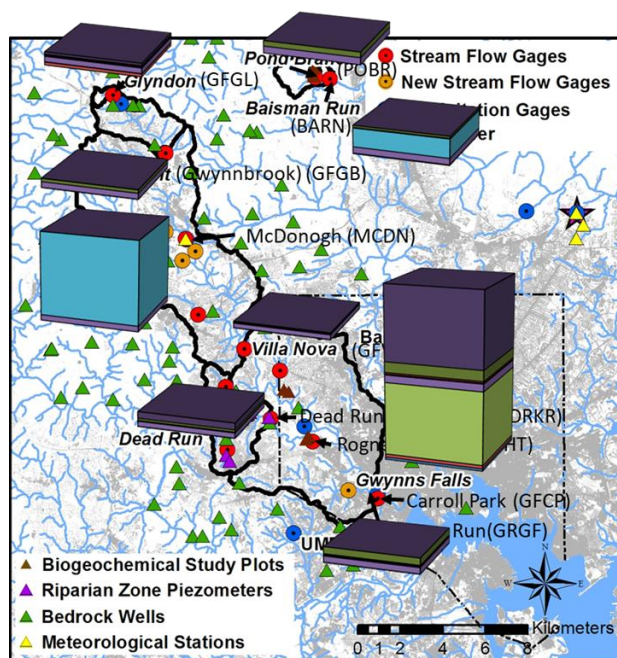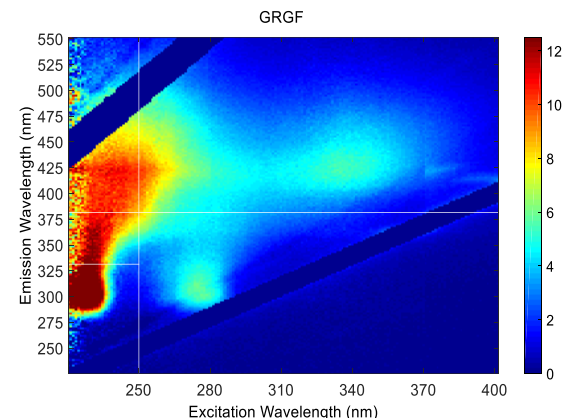
4-MBC: 112 ± 12 ng/g

[He *et al.*, 2017]

Conclusions

Concluding thoughts

1. Fluorescence EEMs represent a quick and easy approach to identify locations of interest in urban streams for follow-up study with other metrics

2. CECs are present in *unimpacted* urban streams, and we posit that the source of these contaminants is leaking wastewater infrastructure

3. Antibiotics, estrogens, and UV-filters were detected throughout the watershed; antibiotic concentrations varied with space and time, but UV-filters were fairly consistent

4. Synthetic estrogens and UV-filters accumulate in aquatic organisms and may disrupt urban ecosystems

A special thanks

Sample collection

Baltimore Ecosystem Study LTER

Center for Urban Environmental Research and Education

Funding sources

UMBC Office of Undergraduate Education

NSF Environmental Engineering (1510420)

NSF Career Award (1653726)

USDA Forest Service

Student Support

Meyerhoff Scholars Program;

MARC U*STAR Program

Thanks for your attention

Any questions?