UV filter occurrence in Chesapeake Bay water, sediment, and aquatic organisms

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The National Academies of Sciences, Engineering, and Medicine

Environmental Impact of Currently Marketed Sunscreens and Potential Human Impacts of Changes in Sunscreen Usage

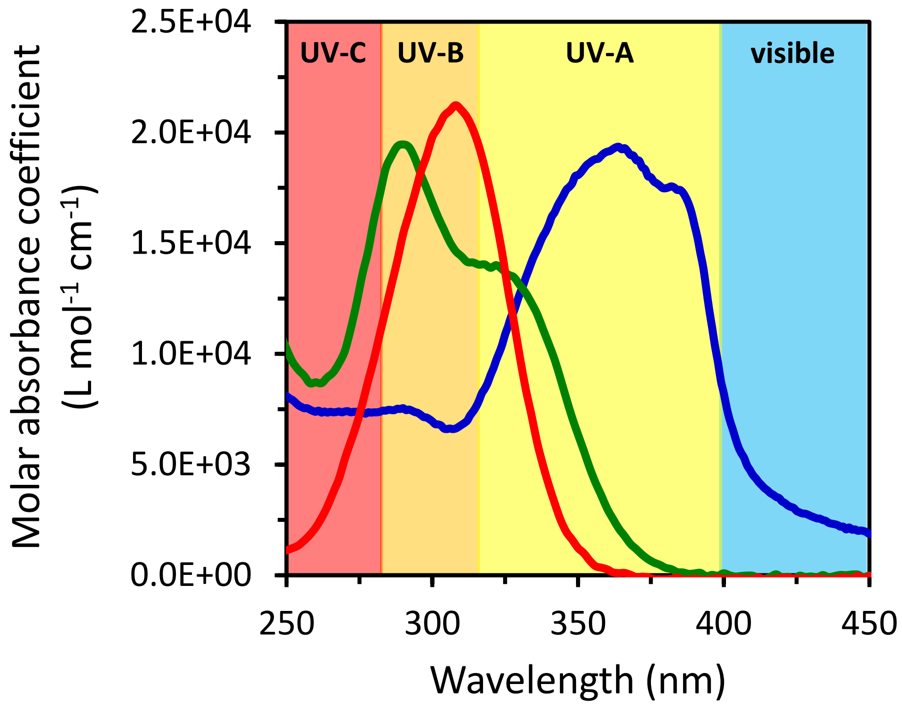
May 27, 2021

UMBC

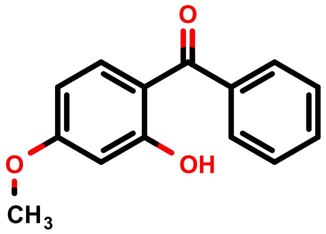
UV filters are the active ingredients in sunscreens and other personal care products that protect skin from UV radiation

Organic UV filters (*e.g.*, oxybenzone, avobenzone) play a crucial role in preventing skin cancer by absorbing harmful UV-A and UV-B light, whereas inorganic UV filters (*e.g.*, TiO_2, ZnO) block light from interacting with skin.

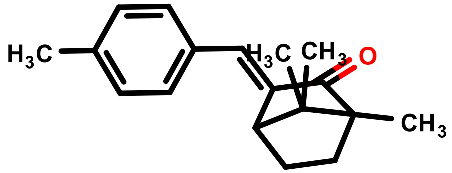
active ingredients



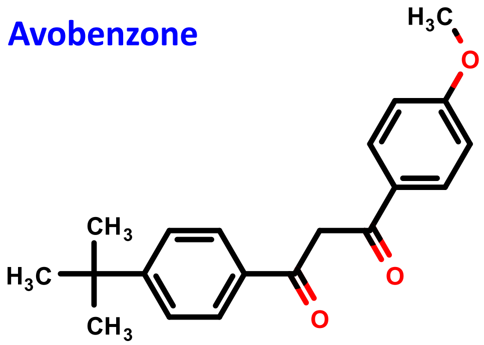
Oxybenzone



4-methylbenzylidene camphor

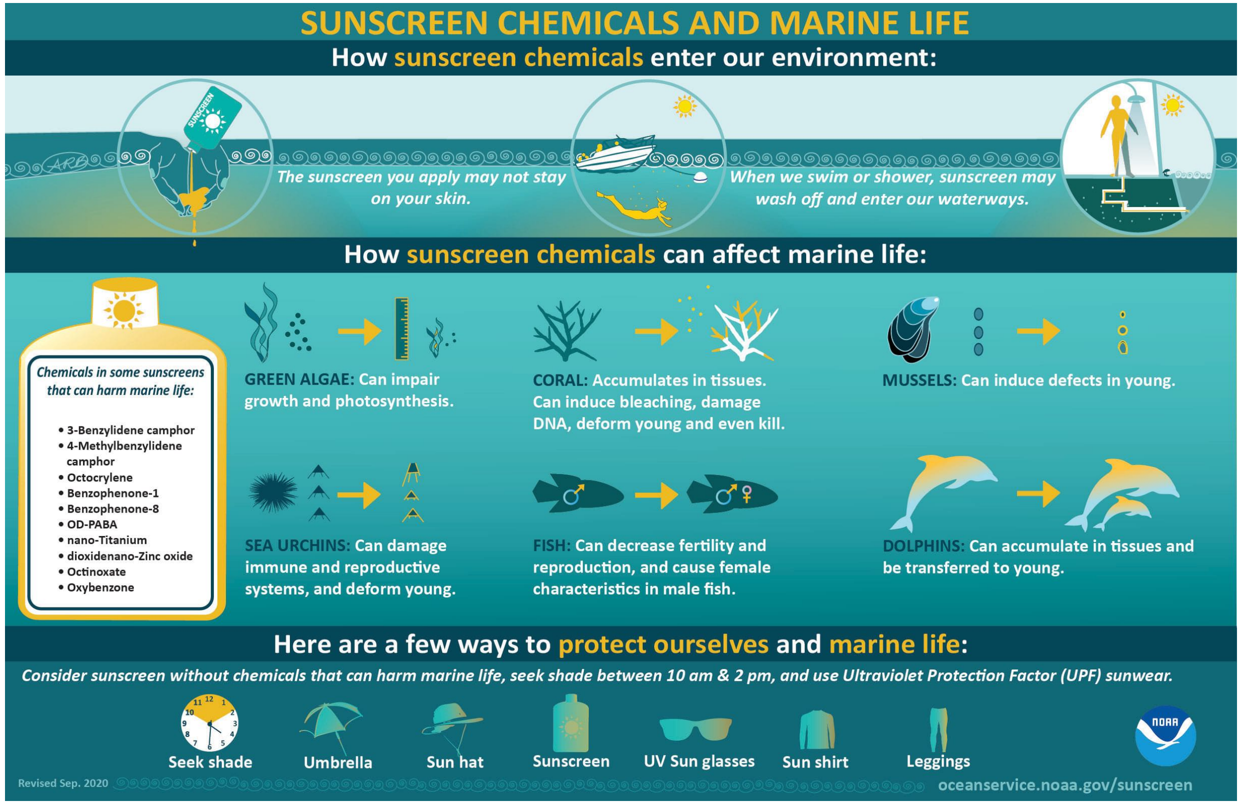


Avobenzone



Recent studies have suggested that UV filters are toxic to a wide range of aquatic organisms

Sunscreens wash off of skin and, ultimately, enter the environment. Negative outcomes have been reported for algae, mussels, sea urchins, fish, and corals.



(NOAA, 2020)

Calicoblast cells exposed *in vitro* to oxybenzone.

Coral species	LC_{50} (µg/L)	95 % CI	LC_{20}	95 % CI
Indo-Pacific species				
Stylophora pistillata (light)	42	28; 60	2 µg/L	1.14; 3.61
Stylophora pistillata (dark)	671	447; 984	14 µg/L	7; 26
Pocillopora damicornis	8	4.96; 12.15	62 ng/L	24; 136
Caribbean-Atlantic species				
Acropora cervicornis	9	5.4; 14.5	63 ng/L	22; 150
Montastrea annularis	74	40; 126	562 ng/L	166; 1459
Montastrea cavernosa	52	36; 72	502 ng/L	247; 921
Porites astreoides	340	208; 534	8 µg/L	3; 16
Porites divaricata	36	21; 57	175 ng/L	60; 420

"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.*)

These initial reports of UV filter toxicity to corals precipitated bans on the sale of sunscreens containing oxybenzone and octinoxate

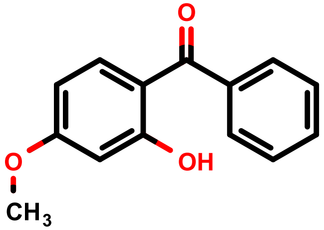
The New York Times

Hawaii Passes Bill Banning Sunscreen That Can Harm Coral Reefs

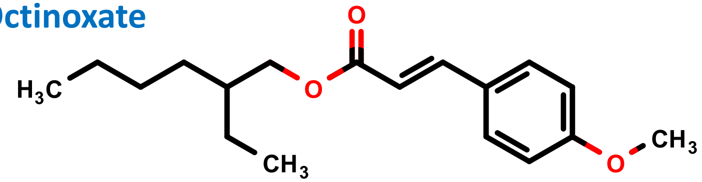
May 3, 2018

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

Oxybenzone



Octinoxate



My objectives for today's talk

1. Discuss some of our advances in the development of multi-residue analytical methods for UV filters in water, sediment, and tissue samples

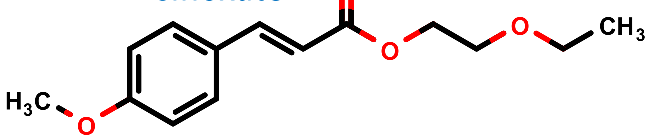
2. Highlight the use of those methods to measure UV filter concentrations in the Chesapeake Bay watershed

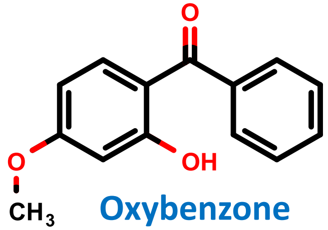
3. Identify opportunities for UV filters to serve as wastewater indicators in settings with less conventional sources (*e.g.*, septic systems, leaking sewers)

Fourteen organic UV filters are approved for use in the United States, and these compounds are often used in combinations of 3-5

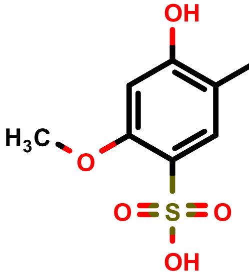
UV filters do not demonstrate the same structural similarity as other contaminant classes (*e.g.*, antibiotics), although there are sub-groups with conserved features (*e.g.*, benzophenone, salicylate, cinnamate).

Cinoxate



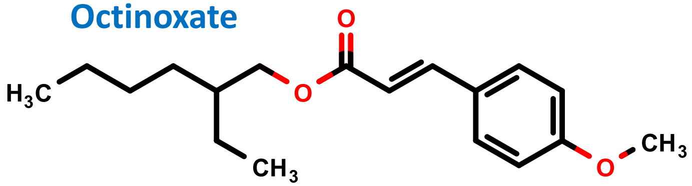


Oxybenzone

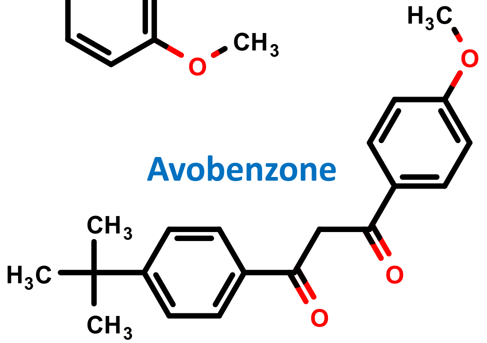


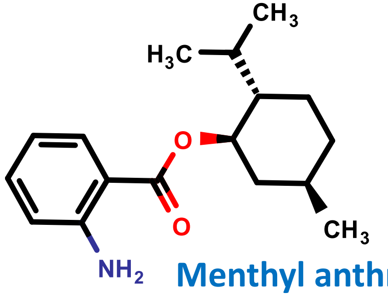
Sulisobenzone

Octinoxate

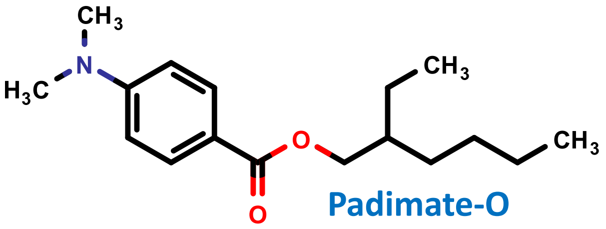


Avobenzone

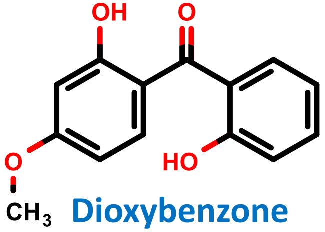




Menthyl anthranilate

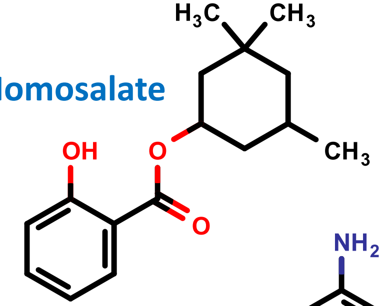


Padimate-O

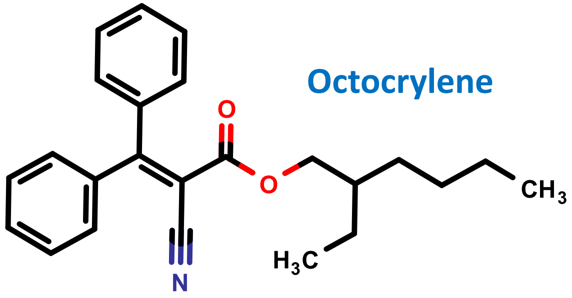


Dioxybenzone

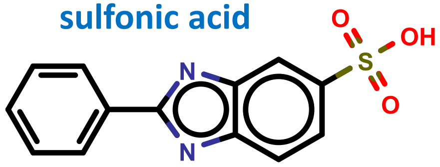
Homosalate

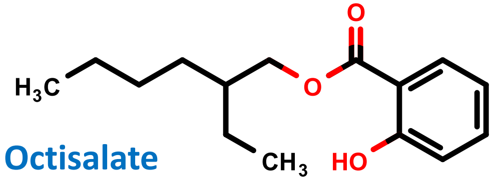


Octocrylene

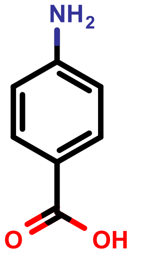


Phenylbenzimidazole sulfonic acid

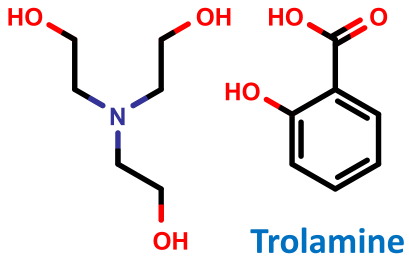




Octisalate



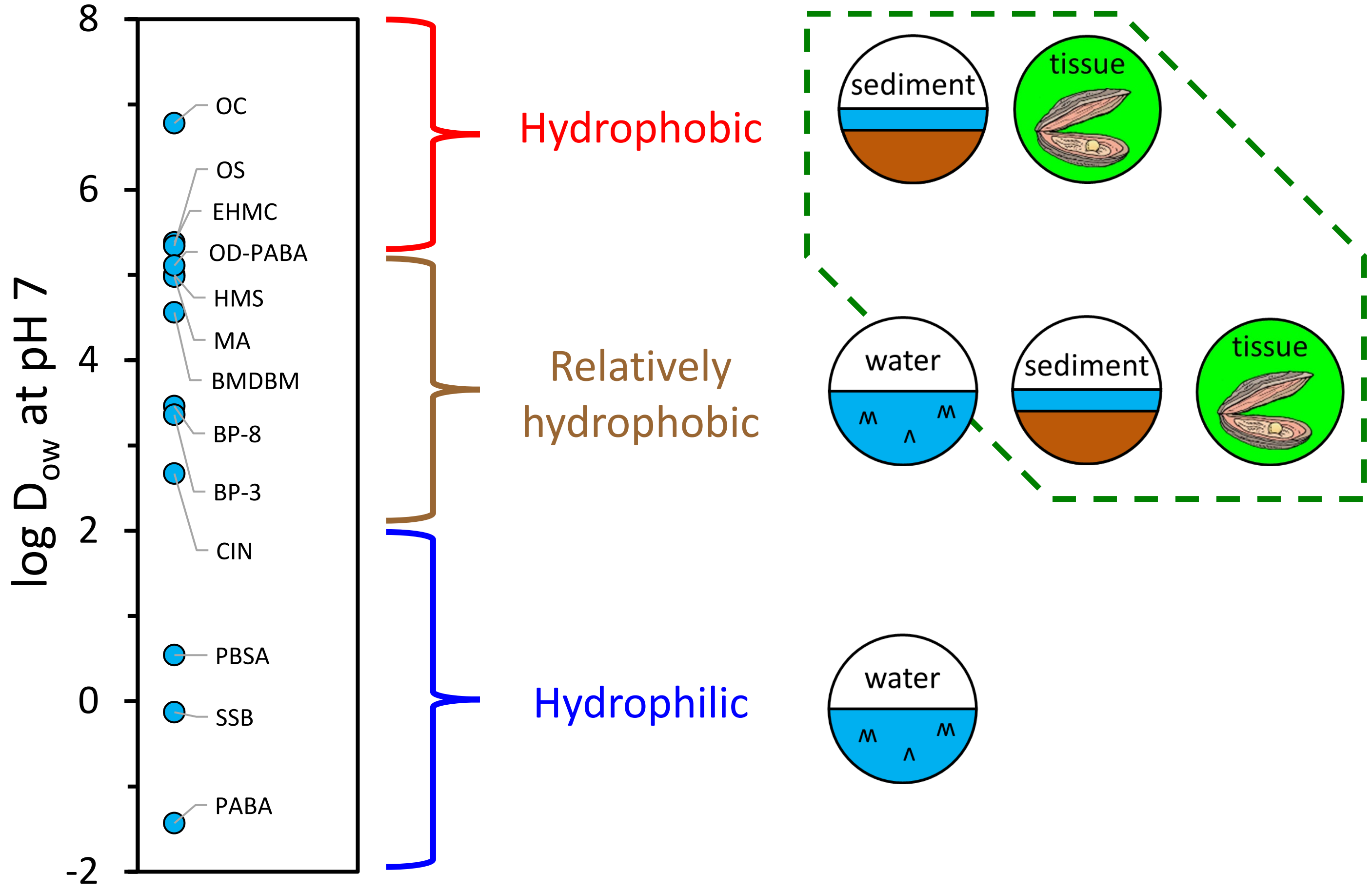
Aminobenzoic acid



Trolamine salicylate

Due to their structural diversity, UV filters exhibit a wide range of partitioning between water, sediment, and tissue

The log D_{ow} values for UV filters at pH 7 show that partitioning between octanol and water varies over eight orders of magnitude for octocrylene (OC) and *p*-aminobenzoic acid (PABA).

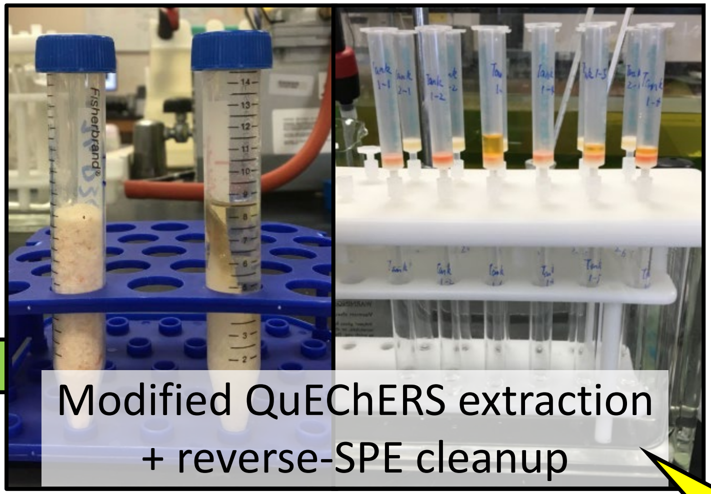


The variable partitioning behavior complicates efforts for concurrent analysis of the full suite of approved UV filters in sediment and tissue matrices.

New extraction and analytical methods needed

UV filters were extracted from water, sediment, and tissue samples to remove interferences and concentrate analytes for measurement

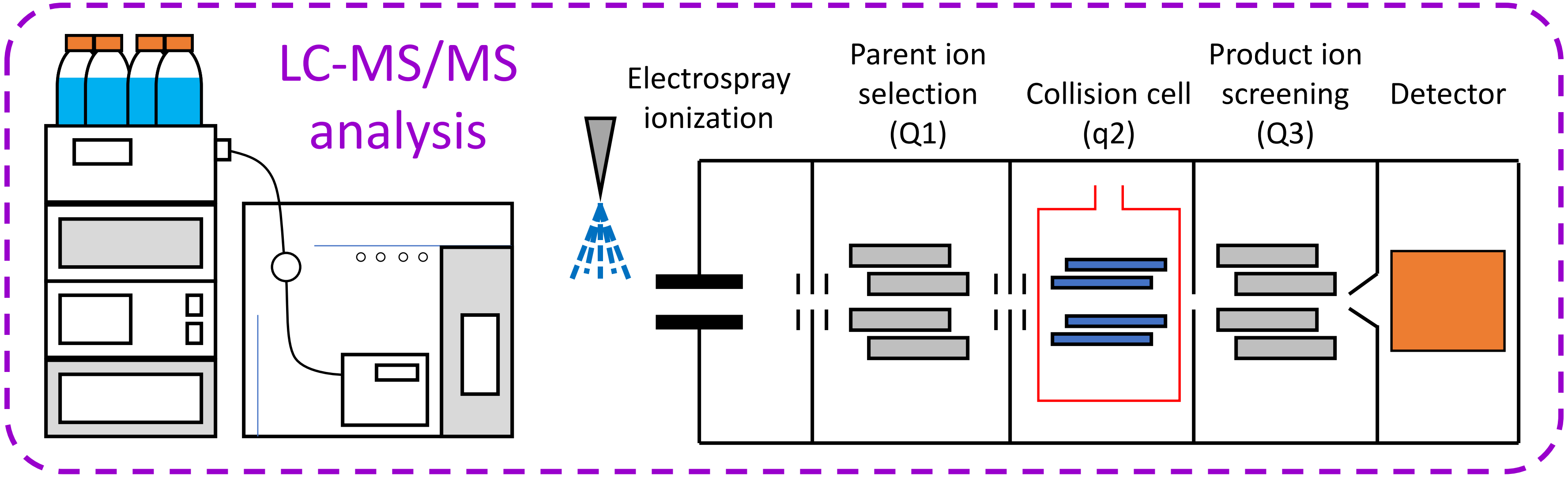
water



tissue
sediment

focus

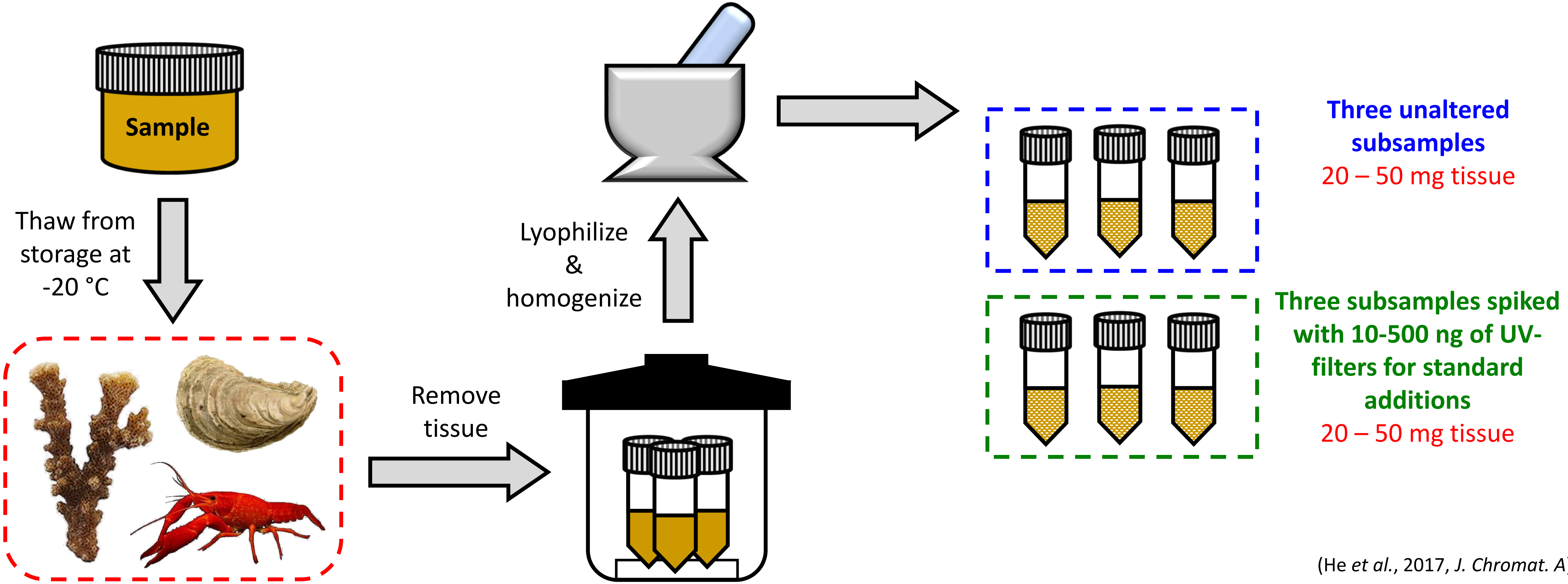
extracts



Preparing tissue samples for quick, easy, cheap, effective, rugged, and safe (QuEChERS) extraction of UV filters and other contaminants

Sample preparation

Tissue was removed from the organism, lyophilized, and homogenized. Then, we generated three unmodified subsamples and three subsamples spiked with analytes for standard additions analysis.



(He *et al.*, 2017, *J. Chromat. A*)

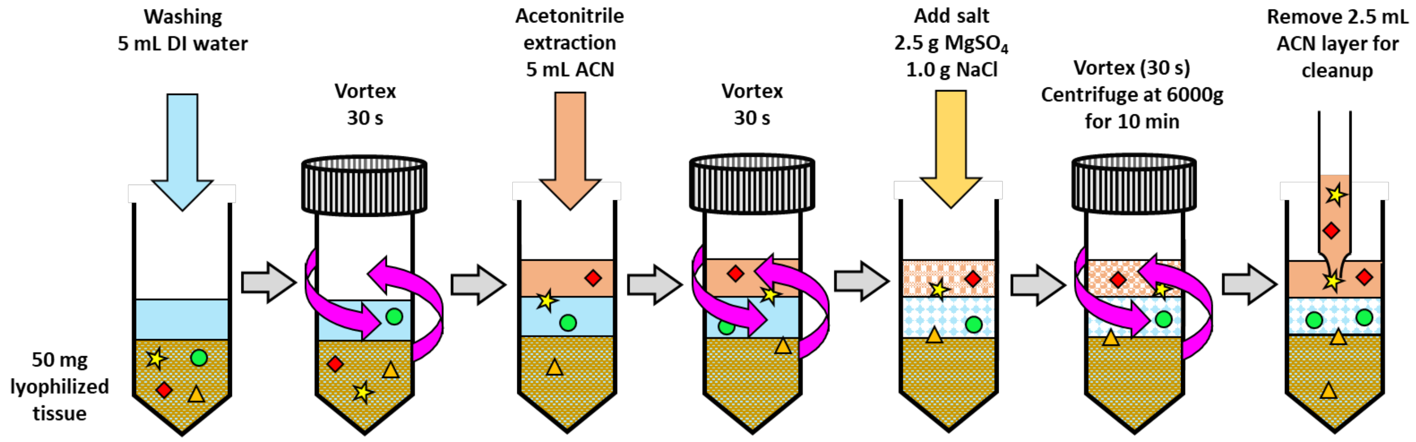
A modified QuEChERS protocol was developed to effectively extract diverse UV filter analytes from tissue samples

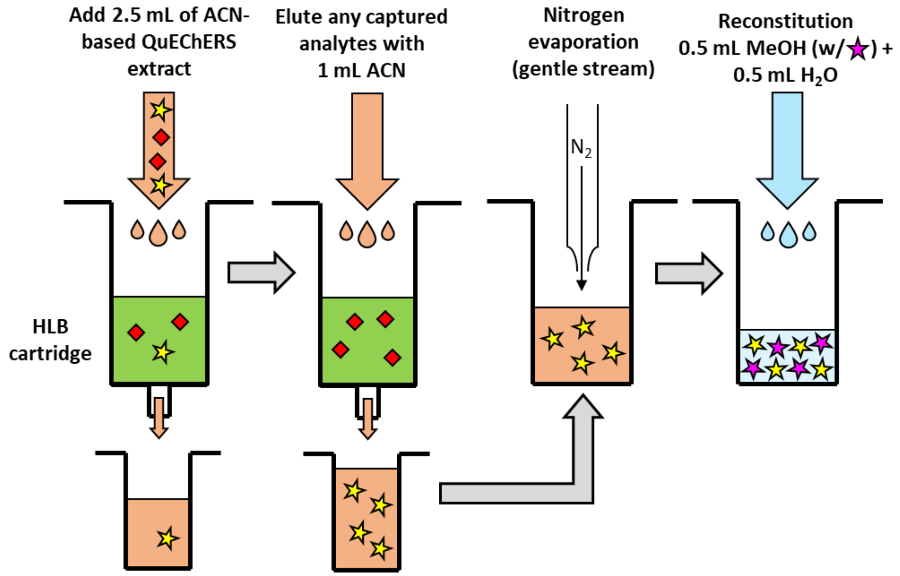
Extraction

Lyophilized subsamples (three original, three with standard additions) were introduced to a modified QuEChERS extraction, which enabled UV filter extraction into the organic phase due to solvent and salting out effects.

Cleanup

QuEChERS extracts still contained interfering substances, but these were effectively removed by reverse-SPE without affecting UV filter concentrations.





Legend
☆ = Analytes (13 UV filters)
△○◇ = Interfering substances
☆ = Internal standards (7 isotopically-labeled UV filters)

(He *et al.*, 2017, *J. Chromat. A*)

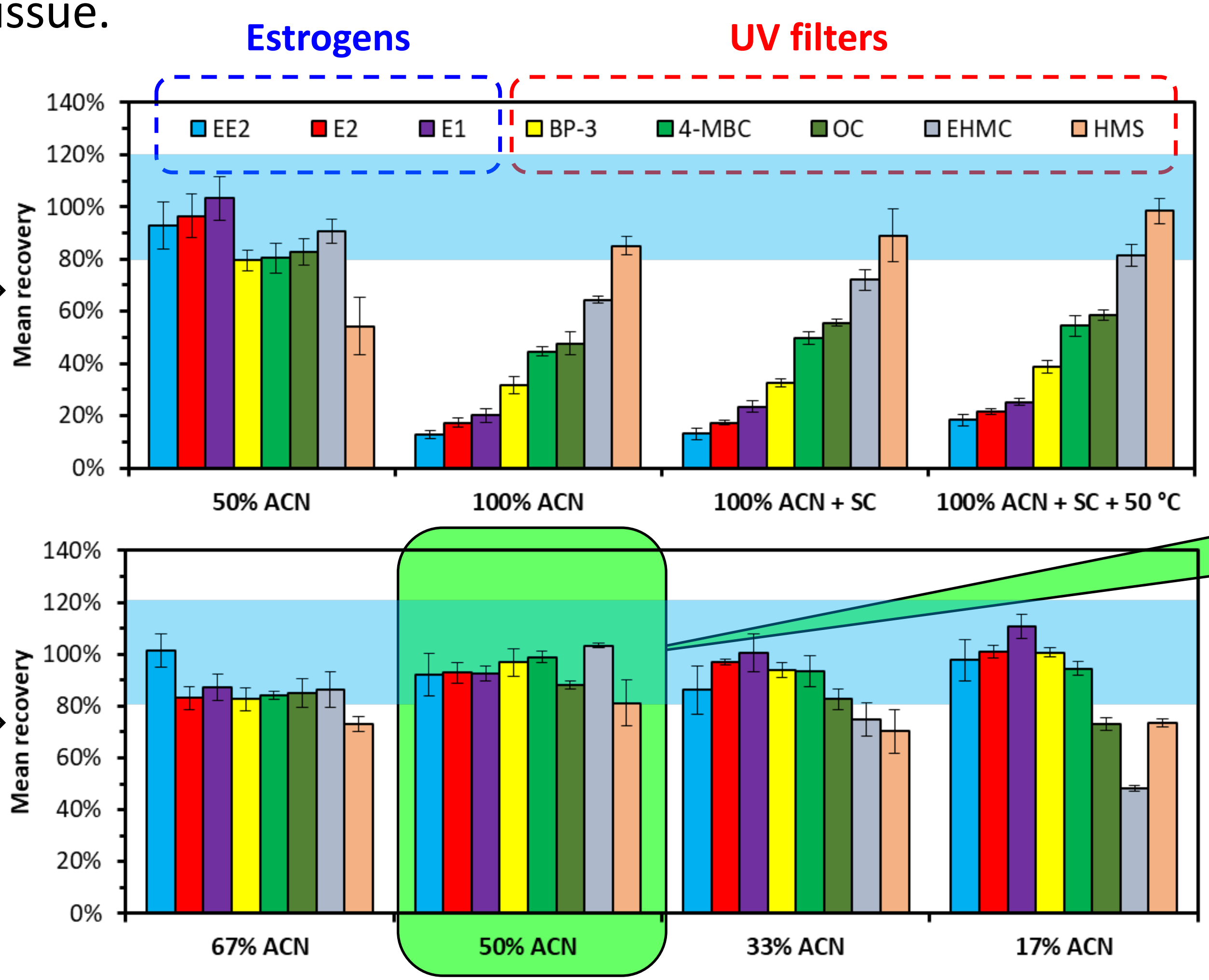
To obtain the above protocols, we conducted a large number of optimization experiments for multi-residue analysis

The variable analyte properties and strong matrix effects complicated extraction, but we achieved > 80% recovery from crayfish tissue.

50 mg tissue w/ 500 ng analytes

50-100% ACN with and without sonication and heat did not provide satisfactory recovery of all analytes

To "salt out" the analytes, we added 2.0 g $MgSO_4$ + 0.5 g NaCl per 5 mL DI water



High recovery of all analytes

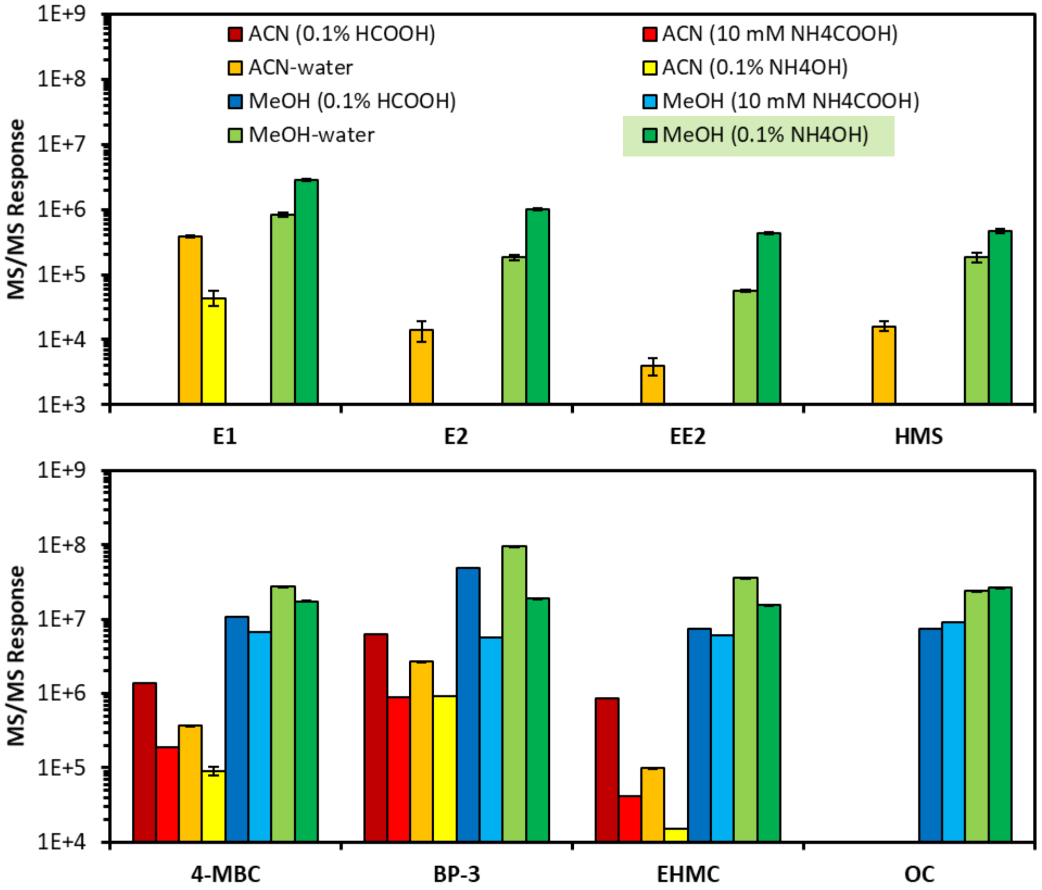
(He *et al.*, 2017, *J. Chromat. A*)

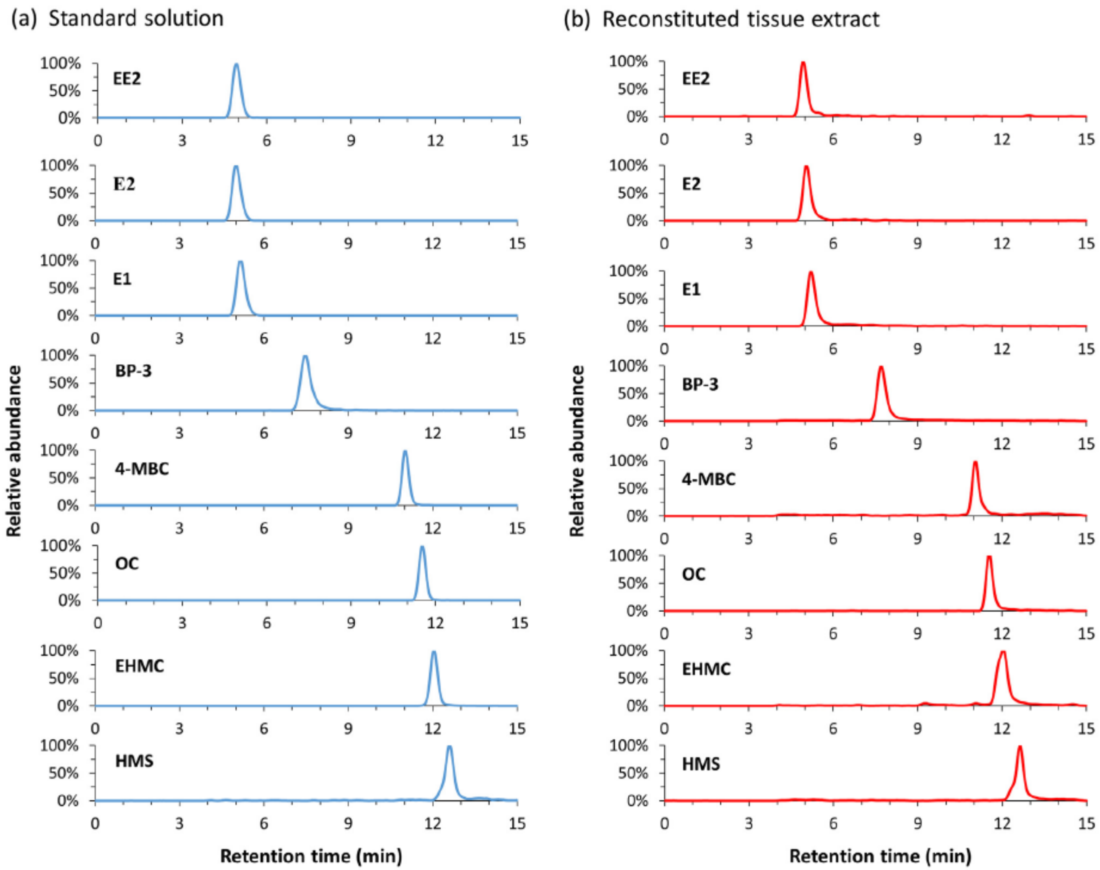
Based on careful study of the LC-MS/MS conditions, we determined that UV filters demonstrate wrong-way-round ionization

In this case, reconstitution with MeOH containing 0.1% NH_4OH was optimal for concurrent ionization (and quantitation) of UV filters and estrogenic hormones. Method detection limits were generally ~1 ng g^{-1} in crayfish tissue.

ESI-

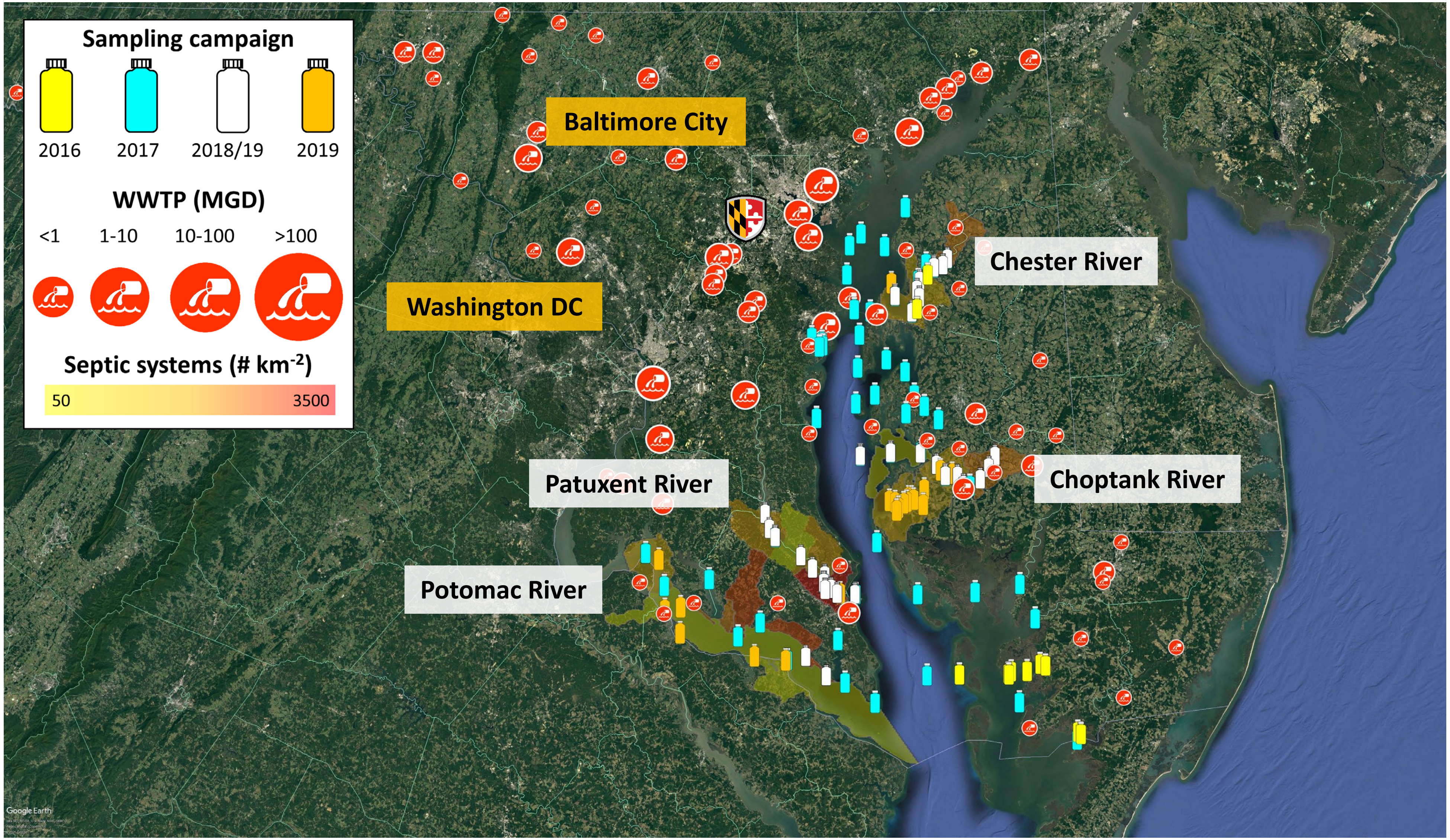
ESI+



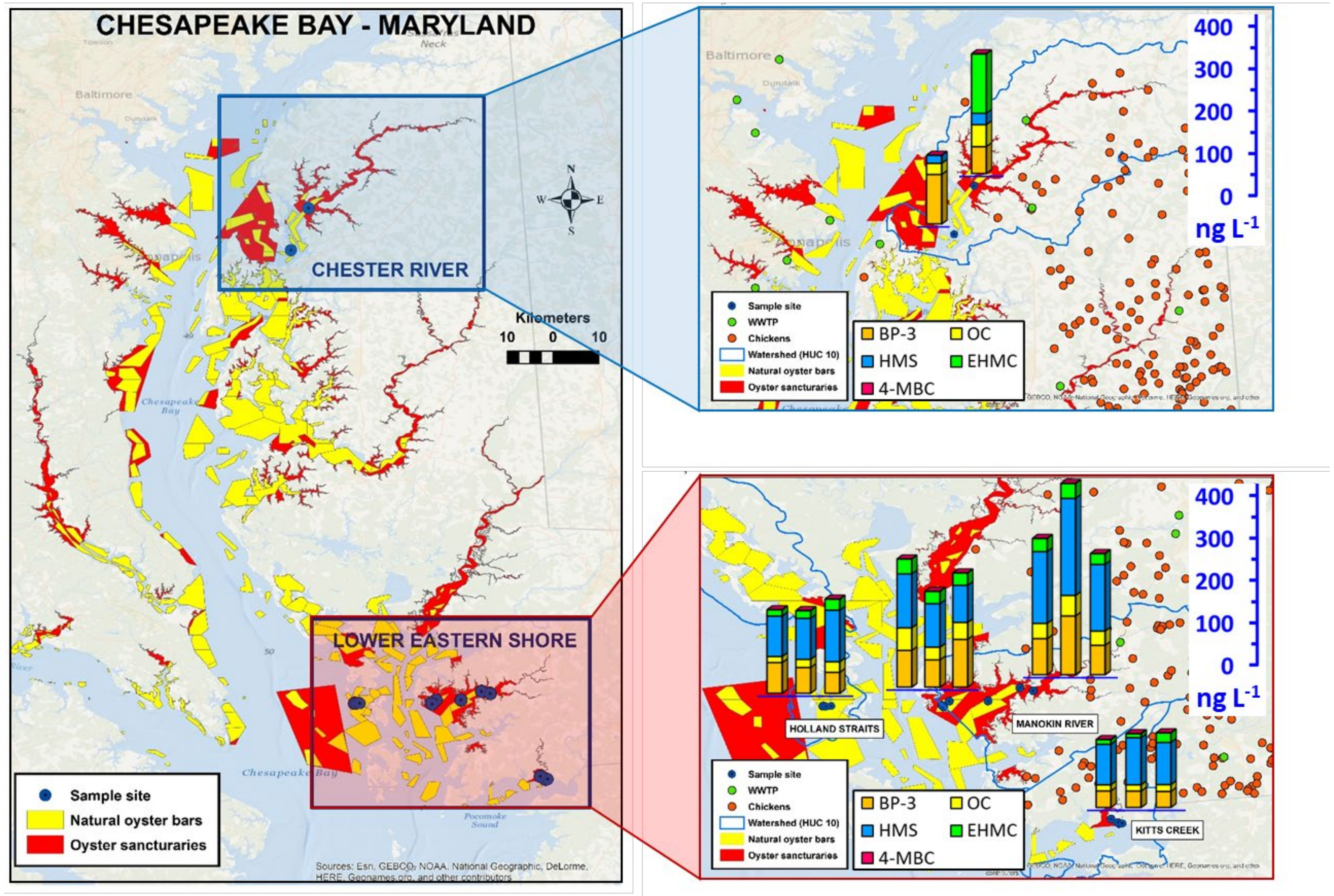


(He *et al.*, 2017, *J. Chromat. A*)

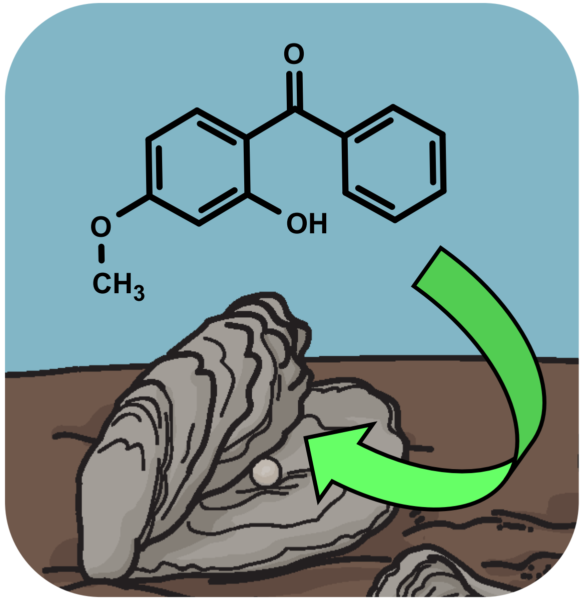
For the past few years, we have been sampling water, sediment, and oysters throughout the Chesapeake Bay



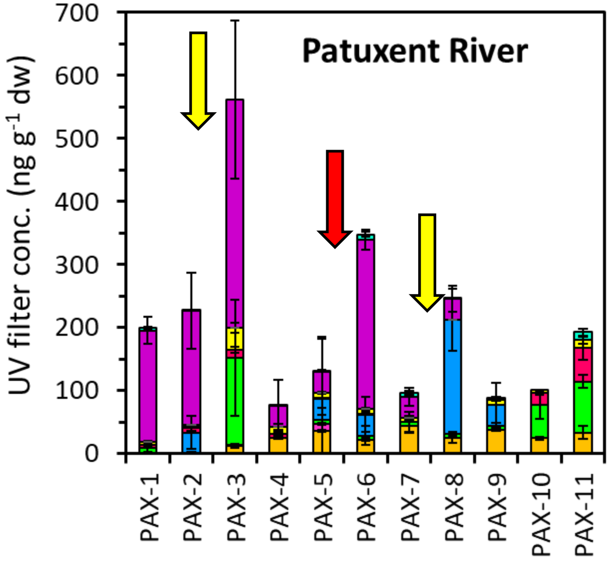
Our first sampling campaign was focused on rural areas with low population density to identify “baseline” concentrations

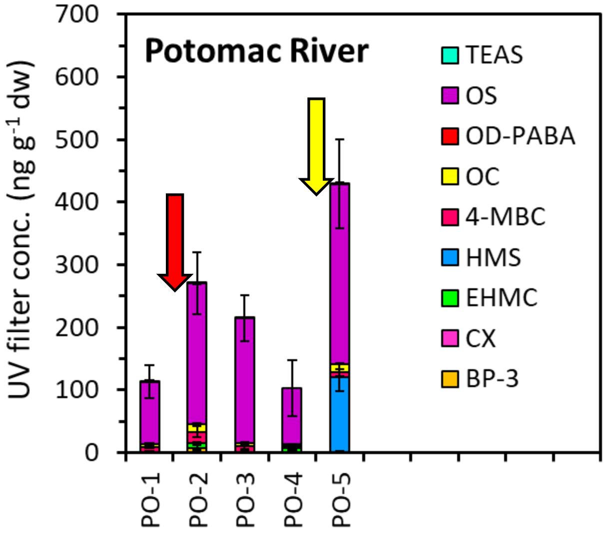


Water-phase concentrations
Oxybenzone (BP-3), octinoxate (EHMC), octocrylene (OC), and homosalate (HMS) were detected at concentrations of 100-400 ng L^{-1}. The data suggest the ubiquitous presence of UV filters in the Chesapeake Bay and potential uptake in oysters.



UV filter concentrations in **oyster tissue** showed clear influences from wastewater treatment plants & other "unknown" sources

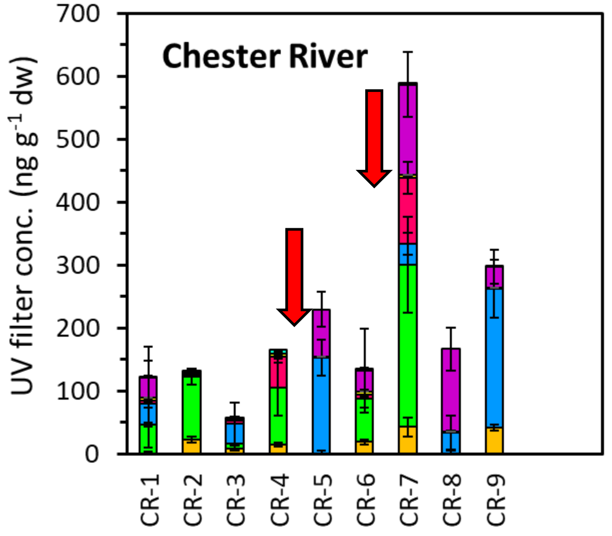


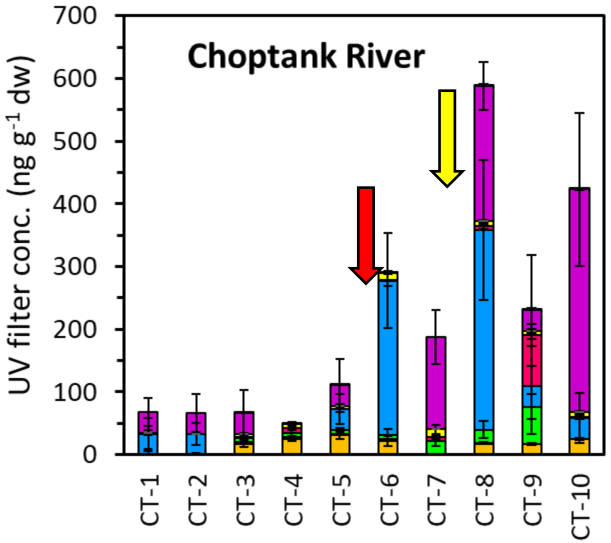


WWTPs

Other

The UV filter concentrations in oyster tissue increased downstream of wastewater treatment plant (WWTP) discharges. However, other sources were suspected based on the presence of other peaks.





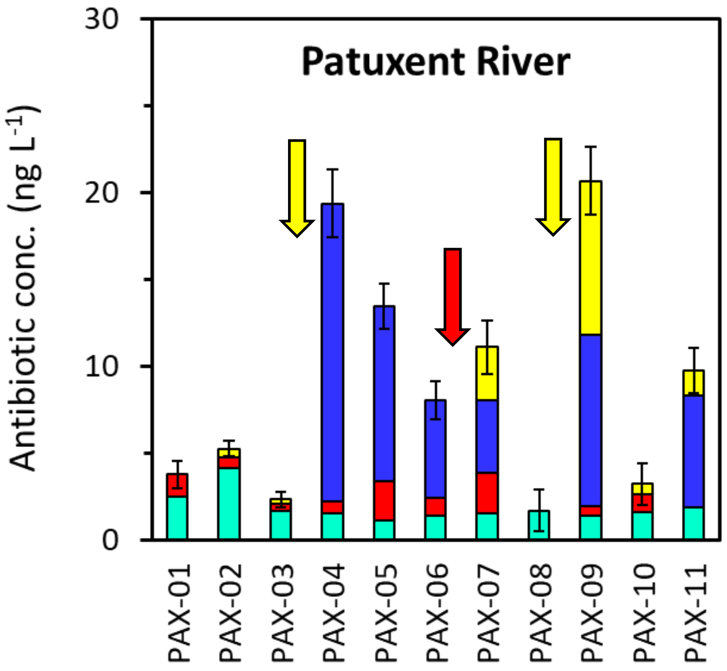
Special thanks to our collaborators

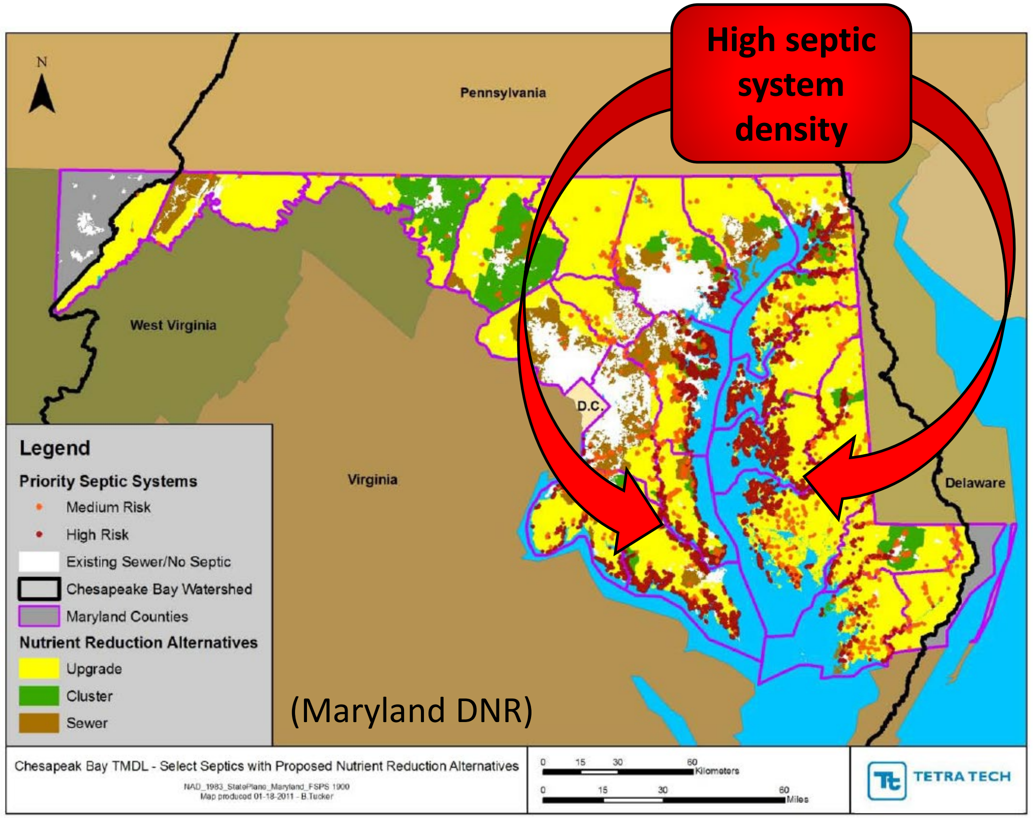
MARYLAND DEPARTMENT OF NATURAL RESOURCES

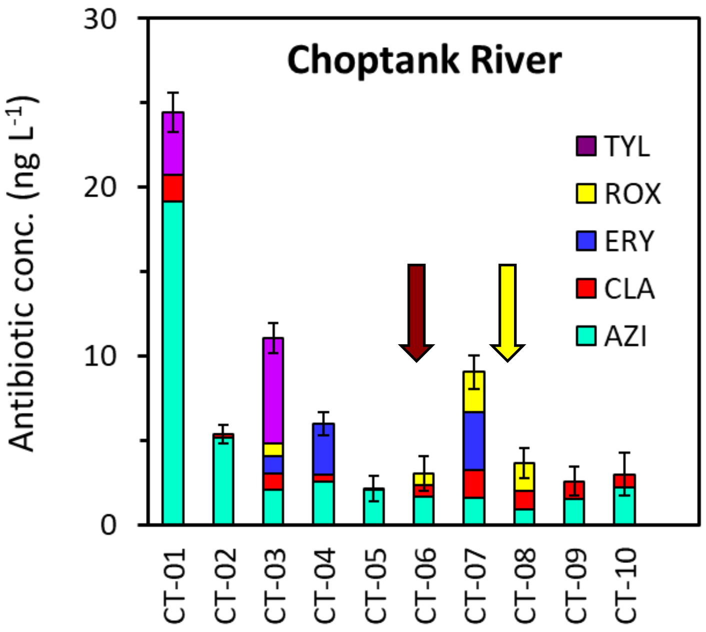
FOREST SERVICE U S DEPARTMENT OF AGRICULTURE

Antibiotic (macrolide) levels in the **water phase** demonstrated similar influences of WWTPs and "unknown" sources

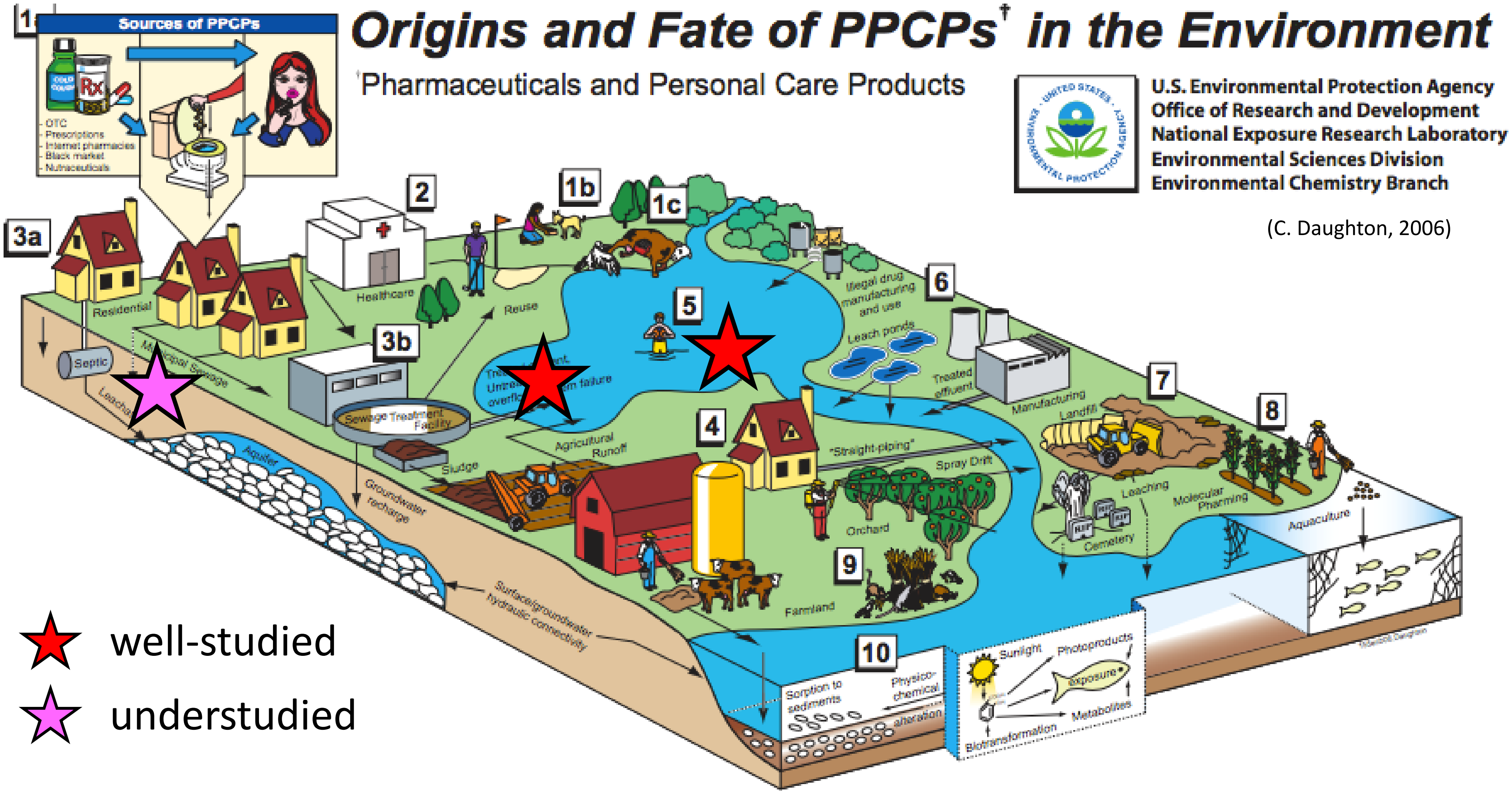
These river systems have a higher density of septic systems, and our ongoing data analysis suggests that these systems may constitute the "unknown" sources of UV filters and antibiotics into these Chesapeake Bay river systems.







The potential importance of septic systems as CEC sources in the Chesapeake Bay watershed motivated us to check other assumptions



(C. Daughton, 2006)

★ well-studied

★ understudied

Wastewater leaks and sanitary sewer overflows are common in urban areas, potentially serving as a source of UV filters (and other CECs)

Wastewater doesn't always go to the wastewater treatment plant.

Baltimore Sun

Baltimore launches live map of sewage pollution — and temporarily stops alerting the public to contamination

More than 14 million gallons of sewage-tainted water has washed into ... spill sewage into the Jones Falls when the system is overwhelmed.

Mar 18, 2019

Chesapeake Bay Magazine

1.3 Million Gallons of Sewage Floods Baltimore Harbor

According to Blue Water Baltimore, Baltimore City's riverkeeper organization, 1.3 million gallons of sewage spilled into the Jones Falls, and in ...

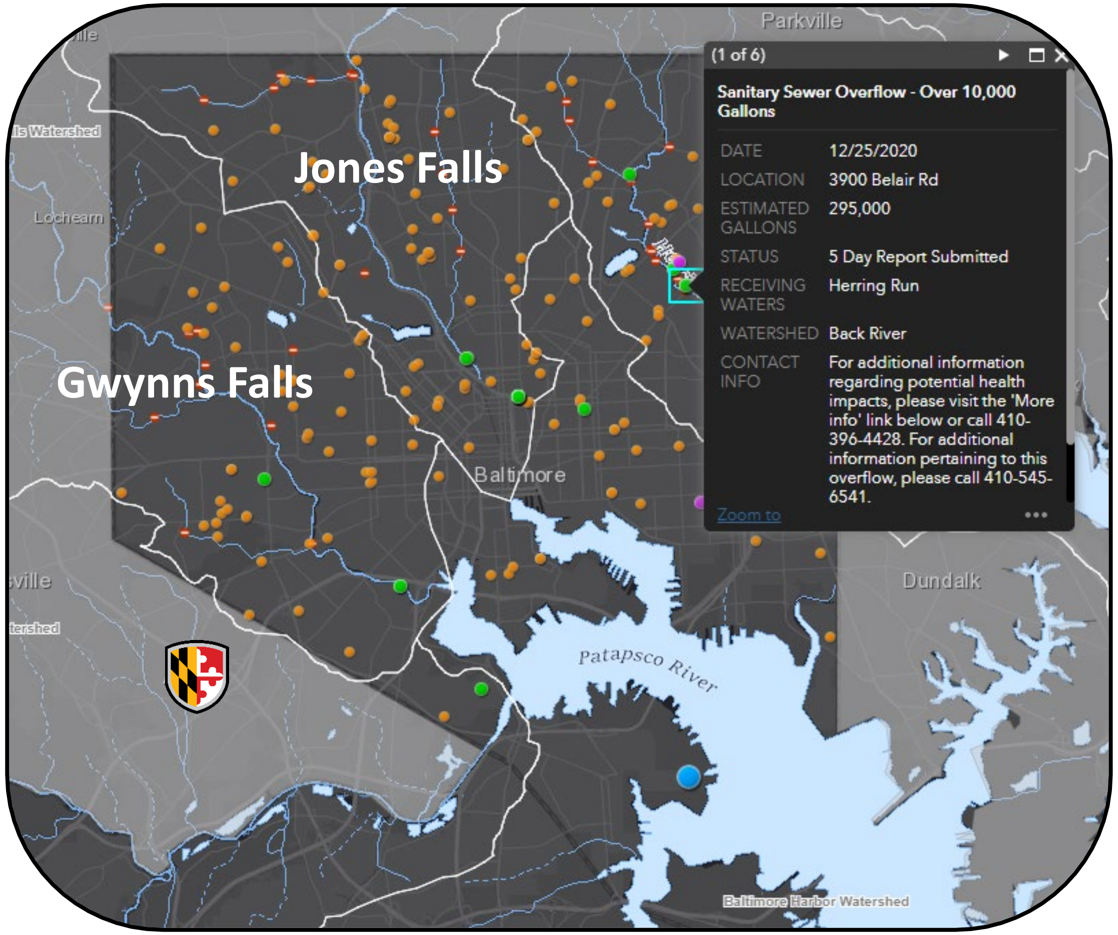
Jul 9, 2019

Chesapeake Bay Magazine

St. Marys River Sewage Overflow Shuts Down Oyster Harvest

The Maryland Department of the Environment (MDE) has announced a nearly month-long emergency closure for shellfish harvesting in a ...

Jan 5, 2021



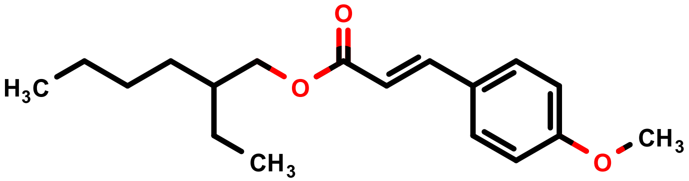
(Baltimore DPW)

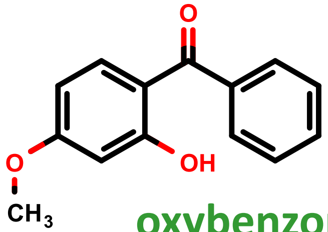
Wastewater effluent is not discharged to this watershed, so uptake of UV filters is hypothesized to stem from leaking sewers and SSOs

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

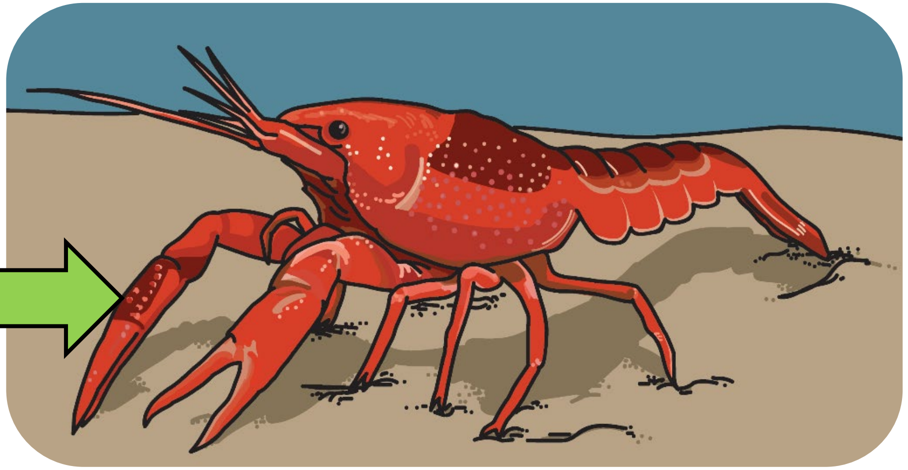
Organism	Site[a]	EE2	E2	E1	BP-3	4-MBC	OC	EHMC	HMS
Eastern crayfish	BARN	n.d.[b]	n.d.	n.d.	n.d.	214 ± 23	60.6 ± 9.0	63.5 ± 7.2	399 ± 48
	DR1	n.d.	n.d.	n.d.	37.9 ± 4.4	352 ± 12	5.0 ± 0.1	n.d.	113 ± 7
	DR2	n.d.	n.d.	n.d.	n.d.	75.3 ± 11	37.1 ± 3.9	83.0 ± 5.1	263 ± 43
	DR3	n.d.	n.d.	n.d.	51.4 ± 2.2	97.8 ±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

octinoxate





oxybenzone



(He *et al.*, 2017, *J. Chromat. A*)

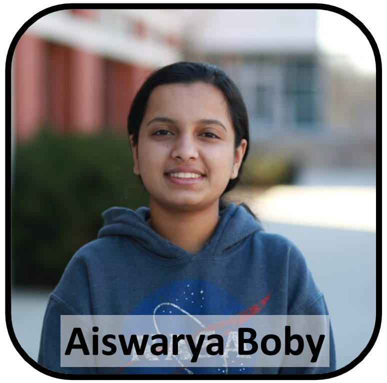
Concluding thoughts

1. Extraction, cleanup, and analytical advances were developed to measure a full suite of UV filters in environmental water, sediment, and tissue samples

2. The occurrence of UV filters in oysters from Chesapeake Bay river systems coincided with wastewater discharges and other “unknown” sources, highlighting potential impacts of septic systems on contaminant concentrations (ongoing work)

3. Leaking sewers and sanitary sewer overflows in urban watersheds of Baltimore City introduced UV filters to streams and aquatic organisms, like crayfish (ongoing work)

Thanks to our great team at UMBC



Collaborators and funding sources

Maryland Department of Natural Resources (especially Mitch Tarnowski)
Maryland Sea Grant
National Science Foundation, CAREER program
National Science Foundation, Environmental Engineering program
UMBC Undergraduate Research Award program
USDA Forest Service (especially Anne Timm)

Thanks for your attention

Any questions?

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