Evaluating land use impacts on contaminants of emerging concern in Cape Cod Bay estuaries

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1. INTRODUCTION

Rapidly increasing residential and commercial development on Cape Cod has greatly impacted the environment. Groundwater, ponds, streams, estuaries and coastal waters are all showing signs of degradation. Contaminated groundwater carrying nutrients—primarily from septic systems, which serve 85% of Cape residents (Massachusetts EOEA 2004)—visibly impairs the health of Cape Cod ponds, estuaries, and coastal waters. The excess nutrients cause algae growth that depletes dissolved oxygen, chokes out native eelgrass, and degrades fish and shellfish habitat.

These inputs of nutrient-rich water also carry other potentially harmful contaminants. Broadly called contaminants of emerging concern (CECs), these contaminants include pharmaceuticals, personal care products, household cleansers and flame retardants. Starting in the early 2000s, a growing body of evidence has shown that CECs are present in surface waters and drinking water across the U.S., particularly in wastewater-impacted systems (Benotti et al. 2009; Kolpin et al. 2002). Some CECs are known to cause endocrine (hormone) disruption, cancer, and effects on development and reproduction. While some of these chemicals are removed or degraded in septic systems (Conn and Siegrist 2009) and wastewater treatment plants (Oulton et al. 2010), many are present in wastewater effluent that can be discharged into the coastal environment (Gaw et al. 2014).

Research by Silent Spring Institute (SSI) has documented CECs in septic systems, groundwater, ponds, and public and private drinking water wells throughout Cape Cod (Rudel et al. 1998; Schaider et al. 2016; Schaider et al. 2014; Standley et al. 2008; Swartz et al. 2006). The most frequently detected types of chemicals include: prescription medications, such as sulfamethoxazole and carbamazepine; organophosphate flame retardants, such as TCEP; per- and polyfluoroalkyl substances, such as PFOS and PFBS; and an artificial sweetener, acesulfame. Ponds and drinking water wells with higher nitrate levels and more extensive nearby land development—both indicators of septic system impact—had higher levels of CECs. A recent review paper (Schaider et al. 2017) synthesized published studies on CECs in septic systems found that while septic systems effectively remove some CECs in household and commercial wastewater, others are only partially removed and can be discharged into groundwater systems.

Building on SSI's work, in 2010 the Center for Coastal Studies (CCS) expanded its coastal water quality monitoring program to test whether these same contaminants could enter coastal waters. With initial funding by the MassBays Research and Planning Grant Program in 2012, CCS tested water samples from four estuaries on Cape Cod Bay for five CECs. This preliminary work focused only on the CECs that were thought to be the most prevalent and/or persistent in the environment and therefore the most likely to be detected. Four of these five CECs were detected, and over half of the samples contained at least one of these four CECs (Costa and Hughes 2012). This study was the first to document the presence of CECs in the coastal waters of Massachusetts. Testing by CCS in 10 estuaries in Nantucket Sound in 2013 for a broader suite of CECs found an additional nine detected CECs. At least one CEC was detected at all sites, with a maximum of nine CECs detected at a site (Costa 2014).

In general, far less research on CECs in coastal waters and sediments. Gaw et al. (2014) reviewed the growing body of studies on pharmaceuticals in coastal and marine environments and found that most commonly used pharmaceuticals have not been analyzed in these environment. The authors concluded that there was a "critical knowledge gap" in information about the potential ecological impacts of pharmaceuticals in coastal and marine environments, which include ecotoxicity and antibiotic resistance. Phillips et al. (2016) analyzed wastewater-related compounds, including hormones, surfactants, fragrances, and organophosphate flame retardants in 79 sites in New York and New Jersey estuaries after Hurricane Sandy. This study found significant variations in the concentrations of some compounds, such as personal care and domestic use products, with higher concentrations measured in highly urban areas, whereas androgen and estrogen hormones were more similar across sites, pointing to the importance of both sources and site-specific fate and transport processes in determining the presence of these compounds in coastal environments.

2. GOALS

This project will evaluate impacts of anthropogenic stressors, such as wastewater from septic systems, on coastal water quality and fill gaps in our understanding of the types and levels of CECs in Cape Cod Bay estuaries for a range of anthropogenic impact. Results will be transferrable to other estuaries in coastal Massachusetts.

- Characterize concentrations of CECs in water and sediment in Cape Cod Bay estuaries.
- Understand links between land use and CEC concentrations across a gradient of land use density.
- Evaluate relationships between CEC contaminations and other water quality parameters, such as nitrogen, and with land use data.
- Inform future decisions on consumer purchasing, wastewater management, and land use management to minimize potential impacts of CECs on coastal waters.
- Increase public awareness of CECs in our coastal waters.

3. METHODS

3.1. Site selection

Ten sites were selected within eight of the 14 embayments delineated by the Massachusetts Bays National Estuary Program in Cape Cod Bay (Figure 1).

Selection of the ten sites included in this study was based on a preliminary assessment of the embayments using the Watershed Multi-Variant Planner (MVP) developed by the Cape Cod Commission (http://www.watershedmvp.org). This tool provides information on wastewater flow, nitrogen loading, water use, land use, and wastewater treatment type. Additional information about the size of watersheds/subwatersheds was obtained from the Cape Cod Commission. We also incorporated dissolved inorganic nitrogen (DIN) data from CCS's water quality monitoring samples collected over the previous 6 years (2010-2015). Table 1 presents a summary of these data.

Some of the embayments delineated by Massachusetts Bays National Estuary Program contain more than one watershed. To more accurately characterize the relationships between land use patterns, wastewater loading, and water quality, for those embayments that contained multiple watersheds, the watersheds were analyzed individually rather than grouping them together for the embayment. We only considered watersheds that were included in the WatershedMVP and where there were sampling locations located within a creek emptying into Cape Cod Bay. For instance, in order to ensure that we had comparable sampling locations from each watershed or subwatershed, we did not consider Provincetown Harbor because of the lack of an accessible creek in this watershed.

For two of the embayments, we selected two watersheds within them. Therefore, the ten selected sites represent ten watersheds and eight embayments. The sampling locations within each watershed were selected based on the location within the marsh system (upper to mid marsh), the ease of access, the existence of historical water quality data collected by CCS, and the depth of water. Depth was an important factor because the passive samplers had to be submerged at all times. Because of the tidal range in Cape Cod Bay much of the watershed area is often left dry at low tide. The sites also had to be accessible by wading for logistics of sample collection (sediment and water) and passive sampler deployment.

Sandwich Harbor Embayment

The Sandwich Harbor Embayment is located entirely within the Town of Sandwich. Also known as Old Harbor, this system is an extensive salt marsh with many tributaries flowing into Old Harbor Creek. As with Scorton, the MEP study of this estuary concluded that this system is not showing any nitrogen impairment of habitat and is a fully functional tidal salt marsh, able to assimilate additional inputs of nitrogen with no degradation to water quality (Howes et al. 2015). The sampling location for this study was in the upper marsh in the tributary flowing under Dewey Avenue.

Scorton Harbor Embayment

The Scorton Harbor Embayment is located entirely within the Town of Sandwich. Scorton Creek flows through an extensive marsh system and empties directly into Cape Cod Bay. The MEP study of this estuary concluded that this system is functioning as a healthy salt marsh and could withstand additional nitrogen loading without water quality impairment (Howes et al. 2013). The sampling location for this study was in the upper marsh at the culvert on Jones Lane.

Sesuit Harbor Embayment

The Sesuit Harbor Embayment is located entirely within the Town of Dennis. Sesuit Creek is a part of a marsh system that empties into Sesuit Harbor. Sesuit Harbor is a harbor of refuge so is routinely dredged to provide access independent of tides. A privately owned marina (Northside Marina) as well as two Town-owned marinas (Sesuit East and Sesuit West) offer over 200 boat slips. Sesuit Creek was the site of a large salt marsh restoration project, completed in 2008 with the replacement and widening of the culvert under Bridge Road, which allowed increased flow to the salt marsh from Sesuit Harbor. The sampling location for this study was located in the mid-marsh at this culvert.

Quivett Creek Embayment

The Quivett Creek embayment is located within the Towns of Brewster and Dennis. It is bordered by the Crowes Pasture Conservation Area. Because nitrogen pollution is not believed to be an issue in this watershed due to a tidal flushing, low intensity development, or geomorphology, this watershed was not included in the MEP study (Cape Cod Commission 2017b). The sampling location for this study was located in the middle of the marsh, accessible by a walking trail.

Namskaket Creek / Little Namskaket Creek Embayment

There were two sites selected within this embayment, one in the Little Namskaket watershed and one in the Namskaket watershed.

Namskaket

The Namskaket watershed is located within the Towns of Orleans and Brewster. The Tri-Town Septage Treatment Facility is located in the upper Namskaket Marsh watershed. This facility was built in the 1980s and began operation in the 1990s. It was closed in 2016. The MEP study of this system determined that, like Little Namskaket, this system was functioning as a healthy salt marsh and has the capacity to assimilate additional nitrogen without impairment (Howes et al. 2007a). The sampling location for this study was located in the upper region of the marsh, downstream from the Treatment Facility at the culvert under the Cape Cod Rail Trail. Flow was restored in 2007 to the upper marsh with the replacement of an undersized culvert with two larger box culverts.

Little Namskaket

The Little Namskaket watershed is located within the town of Orleans. Two of the effluent fields for the wastewater treatment facility for the Community of Jesus are located within this watershed. The MEP study of this system determined that it was functioning as a healthy salt marsh and has the capacity to assimilate additional nitrogen without impairment to the system (Howes et al. 2007a). The sampling location for this study was located in the upper region of the marsh at the culvert under Skaket Beach Road. This culvert was enlarged in 2007 allowing for increased flow from the Bay into the upper marsh.

Boat Meadow Creek / Rock Harbor Embayment

There were two sites selected within this embayment, one in the Boat Meadow watershed and one within the Rock Harbor watershed.

Boat Meadow

The Boat Meadow watershed is located mostly in the Town of Eastham with a small portion in Orleans near the Route 6 rotary. It is composed of a small tidal creek and an extensive marsh system. Because nitrogen pollution is not believed to be an issue in this watershed due to a tidal flushing, low intensity development or geomorphology, this watershed was not included in the MEP study (Cape Cod Commission 2017a). The sampling location for this watershed was in the middle portion of the marsh near the overpass on Bridge Road.

Rock Harbor

The Rock Harbor watershed is located within the Towns of Eastham and Orleans. A tidal creek runs through an extensive salt marsh and empties into in inlet that has been significantly modified to create a harbor. This area is routinely dredged to allow for navigation. Rock Harbor is the only harbor into Cape Cod Bay for the Towns of Eastham and Orleans and supports commercial and recreational boating as well as a large charter fishing fleet. The most inland feature of this estuary system is Cedar Pond, a highly impaired brackish pond (Eichner et al. 2013). The MEP study of this system determined that the upper reaches of the salt marsh show high habitat quality, but there is significant impairment in the lower embayment (harbor) region (Howes et al. 2007b). The sampling location for this watershed was downstream of the culvert between Cedar Pond and Rock Harbor Creek, at the convergence of the Rock Harbor Stream and Cedar Pond subwatersheds. Because the water flowing through the culvert was coming directly from Cedar Pond, data for the Cedar Pond subwatershed are used in this report.

An additional water sample was collected directly from an effluent pipe that empties into Rock Harbor that drains the wetlands adjacent to the Rock Harbor parking lot.

Wellfleet Harbor Embayment

The Wellfleet Harbor embayment is located mostly in the Town of Wellfleet with small portions extending into Truro and Eastham. This watershed is divided into several subwatersheds. The MEP study conducted between 2005-2011 determined that overall, the Wellfleet Harbor estuary system supports “high quality to moderately impaired habitat, with regions of moderate to significant impairment found only in Duck Creek” (Howes et al. 2016).

The natural siltation in Duck Creek has been accelerated by anthropogenic changes to this system including the filling of wetlands, construction of dikes, the railroad embankment, the breakwater and the marina. Increased residential and commercial buildings along the Creek also contributed to declining water quality contributing to the closure of shellfishing in the upper reaches of the creek in 1974 and the seasonal closure in the lower reaches in 1982 due to high coliform bacteria (Natural Resources Advisory Board 1995). This sampling effort occurred within the Duck Creek LT10 subwatershed to the north of the railroad embankment.

Pamet River /Little Pamet River Embayment

The Pamet River embayment is located in Truro. It is part of a marsh system that empties into Cape Cod Bay at Pamet Harbor. Pamet Harbor is Truro’s only public harbor, providing commercial and recreational boating access to Cape Cod Bay. The head of the Pamet River is near the ocean, and several overwashes during storm events have introduced seawater from the ocean into the freshwater marsh at the head of this system, the most recent occurring in 2015.

The work done as part of the Massachusetts Estuaries Project (MEP) from 2007-2009 determined that this system has poor to moderate water quality with highest levels of nitrogen in the upper areas of the salt marsh creeks. DIN/DIP ratios of these upper stations indicated an upland source of nitrogen to the marsh (Howes et al. 2010). The upper Pamet, the freshwater portion, is separated from the lower Pamet, a salt marsh estuary, by a tide gate. The sampling location for this watershed occurred on the west side of the tide gate.

3.2. Sample collection

All samples were collected 1-2 hours before low tide. All passive samplers were deployed and retrieved within 1-2 hours of low tide. To avoid/reduce potential contamination all sampling was conducted by the same personnel at all sites, and clean nitrile gloves were worn when handling any samples, bottles or equipment. No personal care products that contained fragrances, DEET, etc. were used by the samplers, nor were the samplers allowed to drink caffeinated beverages, smoke, or expose themselves to any of the compounds that were tested for. Dates of sample collection and passive sampler deployment and retrieval are provided in Table 2.

PFAS sample collection

A water sample for analysis for PFAS was collected at each site in a methanol-cleaned HDPE liter bottle. All sampling bottles were prepared by the Lohmann Laboratory at the University of Rhode Island (URI) and shipped to CCS. A lab blank was prepared at the URI lab along with the sample bottles. Sampling was done by dipping the bottle directly into the water in the center of the flow, making sure to avoid any surface film. The sample bottle was rinsed three times with a small amount of sample water before the sample was collected. Bottles were filled approximately three-quarters full to allow for expansion when freezing. Two sets of samples were collected at each site, one in late August/early September and a second one in late October/early November. All samples were stored in a freezer until they could be shipped overnight on ice back to URI.

PFAS passive sampler deployment

Twelve polyethylene (PE) passive samplers were prepared at URI, packaged in falcon tubes and stored in HPLC reagent grade water for shipping to CCS. These samplers were deployed at each site coincident with the first collection of water samples (late Aug/early Sep). Deployment consisted of removing the sampler from the falcon tube and attaching it with a zip tie (supplied by URI) to mooring at each site. Samplers were deployed for approximately one month and retrieved when the second set of water samples was collected (late Oct/early Nov). After retrieval, they were placed back in the falcon tubes in which they were shipped and stored in a freezer until they were shipped overnight on ice back to URI. Due to problems with the analyses of extracts from these samplers, we were not able to obtain data from these passive samplers. Instead, we analyzed extracts from the POCIS passive samplers (described below) to provide time-integrated PFAS measurements.

Sediment sample collection

All stainless steel equipment (pails and spoons) used for the collection of bed sediment was cleaned with Liquinox, thoroughly rinsed with tap water, and then rinsed with DI water. A final methanol rinse was completed for trace organics level cleaning. At the field site, all equipment was thoroughly rinsed with stream water prior to collection of bed sediment sample.

Once at the site, efforts were made to disturb the sediment as little as possible. Walking down stream, small amounts (spoonfuls) of sediment were collected to composite in the stainless steel pail, trying to collect the finest grained sediment at the site (e.g. silt/clay grain size, <2mm when possible). Sediment samples were composited from multiple depositional locations throughout the sampling site. Once collection was complete, the sample was thoroughly mixed by stirring in the pail to homogenize it, removing as much organic material as possible. The sediment sample was distributed among the three glass amber jars provided for each site, each filled three-quarters full, in order to leave headspace for freezing. All sediment samples were stored in the freezer and shipped on ice overnight to USGS once all sampling was completed.

POCIS deployment

Polar Organic Chemical Integrative Samplers (POCIS), used for measuring hydrophilic organic contaminants, were deployed in mid-August. Deployment was conducted following the guidelines detailed in Alvarez (2010). Six POCIS membranes (41 cm^2 sampling surface area, 200 mg of Oasis HLB each) mounted on 2 holders were prepared and loaded into canisters at the USGS Columbia Environmental Research Center. They were shipped in sealed, clean paint cans. They were stored in a freezer until they day of deployment. The paint cans were opened at the site and immediately placed in the water and secured to a mooring. Samplers were deployed for approximately six weeks. After retrieval, they were immediately placed back in the paint cans in which they were shipped, sealed tightly, and stored in a freezer until they could be shipped overnight on ice back to USGS.

PPCP water sample collection

Water samples were collected in two plastic bottles and two glass vials at each site for analysis of pharmaceuticals and personal care products (PPCPs). Water was collected in the center of flow, avoiding any surface film. For the 2 plastic bottles, the bottles were rinsed three times with sample water and then filled three-quarters full to save room for expansion when freezing. For the two glass vials 10 ml of sample was filtered directly into the vial using syringe filters provided by USGS. All samples were stored in a freezer until they could be shipped overnight on ice back to USGS.

Quality Assurance / Quality Control

In addition to the samples listed above, we collected the following QA/QC samples:

- A duplicate PE sampler was deployed at Duck Creek and Namskaket Creek. The PE sampler at Namskaket Creek could not be retrieved.
- Replicate sediment samples were collected at Pamet River and Sesuit Creek.
- A replicate water sample for PFAS analysis was collected at Namskaket Creek during the first sampling event. A second replicate sample for PFAS analysis was collected at Quivett Creek during the second sampling event.
- A field blank for PFAS was collected at Pamet River by transferring HPLC reagent grade water into a clean blank bottle.

- A replicate water sample for PPCPs was collected at the Old Harbor site.
- A field blank for PPCPs was collected at Little Namskaket Creek by transferring HPLC reagent grade water into a clean blank bottle.
- A travel blank for PFAS was carried to each field site during collection of samples.

3.3. Sample analysis

Samples from each site were analyzed for nearly 200 trace organic compounds. Sediment samples were analyzed for a range of wastewater-related compounds and hormones. Pharmaceuticals and PFASs were analyzed in grab water samples, and PFASs and hormones were analyzed in POCIS passive samplers. A full list of analytes, along with detection limits, is provided in the Appendix.

Sediment Samples

Sediment samples were analyzed for 63 wastewater-related compounds and hormones following USGS Methods SH5433, detailed in Burkhardt et al. (2006) and SH6434 (Hormones), detailed in Foreman et al. (2012). In brief, the wastewater method focuses on the determination of compounds indicative of wastewater, which were chosen on the basis of potential toxicity or endocrine disruption potential. Wastewater compounds include surfactants, fragrances, antioxidants, disinfectants, food additives, plastic components, industrial solvents, PAHs, fecal and plant sterols, organophosphate flame retardants, and high-use domestic pesticides. Three compounds analyzed with the wastewater compound method were also analyzed in the hormones method (bisphenol A, cholesterol, and 3β-coprostanol) that had lower detection limits, so the data for these three compounds are reported as measure using the hormones method.

Sediment and soil samples were extracted using a pressurized solvent extraction system. The compounds of interest were extracted from interfering matrix components by high-pressure water/isopropyl alcohol extraction. The compounds were isolated using disposable solid-phase extraction (SPE) cartridges containing chemically modified polystyrene-divinylbenzene resin. The cartridges were dried with nitrogen gas, and then sorbed compounds were eluted with methylene chloride (80 percent)-diethyl ether (20 percent) through Florisil/sodium sulfate SPE cartridge, and then determined by capillary-column gas chromatography/mass spectrometry.

Recoveries in reagent sand samples fortified at 4 to 72 μg (micrograms) averaged 76±13% relative standard deviation and RLs ranged from 50 to 500 μg/kg for all wastewater compounds. However, RLs for this method are scaled on the basis of the mass used for analysis, and therefore can vary substantially among samples.

Pharmaceuticals in Water

Water samples were analyzed for 109 human-use pharmaceuticals using USGS Method 2440, described in detail by Furlong et al. (2014). This method is used for the determination of a 100-microliter aliquot of a filtered water sample directly injected into a high-performance liquid chromatograph coupled to a triple-quadrupole tandem mass spectrometer using an electrospray ionization source operated in the positive ion mode. The pharmaceuticals were separated by using a reversed-phase gradient of formic acid/ammonium formate-modified water and methanol. Multiple reaction monitoring of two fragmentations of the protonated molecular ion of each pharmaceutical to two unique product ions was used to identify each pharmaceutical qualitatively. The primary multiple reaction monitoring precursor-product ion transition was quantified for each pharmaceutical relative to the primary multiple reaction monitoring precursor-product transition of one of 19 isotope-dilution standard pharmaceuticals or the pesticide atrazine, using an exact stable isotope analogue where possible. Each isotope-dilution standard was selected, when possible, for its chemical similarity to the unlabeled pharmaceutical of interest, and added to the sample after filtration but prior to analysis.

The method detection limit of each pharmaceutical was determined from analysis of pharmaceuticals fortified at multiple concentrations in reagent water. The calibration range for each compound typically spanned three orders of magnitude of concentration. Absolute sensitivity for some compounds, using isotope-dilution quantitation, ranged from 0.45 to 94.1 nanograms per liter, primarily as a result of the inherent ionization efficiency of each pharmaceutical in the electrospray ionization process.

Hormones in POCIS

The method used for the analysis of hormones retained in the POCIS extracts and water samples follow those described by Alvarez et al. (2004) and by Foreman et al. (2012) which uses solid-phase extraction combined isotope dilution quantification method for analysis. This method includes 20 analytes including estrogens, androgens, and additional micropollutants, with reporting limits that range from 0.0004 to 0.004 μg/L for hormones, from 0.100 μg/L for bisphenol A (BPA), and 0.200 μg/L for 3β-coprostanol (COP) and CHO (cholesterol).

Once received at the lab, the POCIS were removed from the deployment canisters and rinsed with DI water to remove any particles. Each POCIS was opened and the sorbent transferred with DI water into pre-cleaned empty solid-phase extraction (SPE) cartridges (25 mL, Biotage, Charlotte, NC). The sorbent was dried by pulling (by vacuum) air through the sorbent bed for 10 min. Once dry, the sorbents were ready for analysis for hormones.

The POCIS for the analysis of hormones were extracted with 25 mL of methanol (Optima grade, Fisher Scientific), which was subsequently evaporated to 2–3 mL by rotary evaporation prior to being combined into a single sample. The samples were concentrated to <1 mL under nitrogen and solvent exchanged into water for analysis by high-performance liquid chromatography/tandem mass spectrometry (HPLC/MS/MS).

Per- and Polyfluoroalkyl Substances (PFASs)

The method for analysis of 13 PFASs was adopted from Benskin et al. (2012). PFASs were determined in water and POCIS extracts by use of isotope-dilution and offline solid phase extraction (SPE) followed by liquid chromatography coupled with triple quadrupole mass spectrometry. The analysis comprises unlabeled and isotope-labeled reference standards of perfluoroalkyl carboxylic acids (PFCAs, C6 to C12: PFHxA; PFHpA; PFOA; PFNA, PFDA; PFUnDA; PFDoDA) and perfluoroalkyl sulfonates (PFSAs, C4, C6, C8, C10: PFBS; PFHxS; PFOS; PFDS), and perfluoroalkyl sulfonamides (FOSA; N-MeFOSAA; N-EtFOSAA).

Water samples were spiked with 3 ng of an isotopically labeled standard mix of PFASs prior to extraction. Samples were extracted using Oasis® solid phase extraction (SPE) weak anion exchange (WAX) cartridge (6-cc barrel size, 150-mg sorbent weight, 30 µm particle size, Waters, Milford, MA). SPE WAX cartridges were first washed with 4 mL MeOH and NH_4OH (0.5%) and then conditioned with 4 mL of pure methanol and 4 mL DI water. Samples were loaded onto SPE cartridges in a vacuum manifold at 1 drop/second and washed with 5 mL DI water. After drying the cartridge under vacuum, PFASs were eluted into 15 mL polypropylene centrifuge tubes with 4 mL of 0.5% ammonium hydroxide in methanol. The eluents were reduced under a nitrogen bath at 40°C to just 750 µL. The extract was reconstituted with 930 µL 0.3% ammonium hydroxide in methanol and 750 µL DI water, vortexed, centrifuged at 13,000 rpm for 20 minutes, and the supernatant was transferred to 2mL autosampler vials. 300 µL of the extract was transferred to a polypropylene microvial for analysis by HPLC-MS/MS. All equipment was rinsed in a basic methanol solution prior to use. Samples were analyzed using an Agilent 6460 triple quadrupole liquid chromatograph tandem mass spectrometer (LC-MS/MS) equipped with a Poroshell 120 EC-C18 column run in the negative ion electrospray (ESI-) mode using multiple reaction monitoring. Additional methodological information is provided in Weber et al. (2017).

Multiple reaction monitoring (MRM) scans in negative ion mode of the molecular ion and the two most predominant fragments for each analyte were utilized. Selected MRM transitions (quantifier and qualifier) for each analyte and internal standard together with retention time matching were used for identification of individual compounds. The ratio of quantifier and qualifier transition in unknown samples was compared to the average ratio of all included standard samples. A generic tolerance of 30% was accepted for positive results.

Other water quality parameters

Several additional water quality parameters were measured at these sites coincident with the collection of data on contaminants. Temperature, salinity and dissolved oxygen were measured in situ using a YSI Pro DSS Handheld. A water sample was taken back to the CCS laboratory to measure plant pigments (chlorophyll a and pheophytin), turbidity, and nutrients (nitrate+nitrite, ammonium, ortho-phosphate, silicate, total and total dissolved nitrogen, total and total dissolved phosphorus, particulate organic nitrogen, particulate organic carbon). For this report, only nitrogen and salinity are incorporated into the analysis.

Dissolved inorganic nitrogen (DIN) was determined by summing the concentrations of nitrate, nitrite and ammonium. An Astoria 2+2 autoanalyzer was used to determine concentrations of these different species of nitrogen. For the analysis of nitrate + nitrite, following EPA method 353.4, nitrate in the sample is reduced quantitatively to nitrite by cadmium metal in the form of an open tubular cadmium reactor (OTCR). The nitrite thus formed plus any originally present in the sample is determined as an azo dye at 540 nm following its diazotization with sulfanilamide and subsequent coupling with N 1 naphthylethylenediamine. These reactions take place in acidic solution. For analysis of ammonium, following EPA method 350.1, the sample is mixed with o-phthaldialdehyde and sodium sulfite in a borate-buffered solution at 75°C. After sufficient mixing, the sample concentration is measured by fluorescence spectroscopy using 360 nm excitation and 420-470 nm emission wavelengths. The increase in fluorescence is directly proportional to the ammonia concentration.

3.4. Data analysis

In addition to reporting concentrations of individual CEC compounds, we developed two metrics to integrate data on multiple analytes within each family of chemicals. We calculated the sum of detected concentrations across all compounds detected at measurable concentrations within a class of chemicals. This method may underestimate the actual total concentration because chemicals that were not detected may still be present at concentrations below the detection limit. We also calculated the number of analytes detected within each chemical family, including compounds that were detected but not quantifiable. These metrics are helpful for characterizing the variations in the levels of chemical families across sites.

We evaluated the associations between CEC concentrations and several indicators of septic system impact: total nitrogen loading estimated for each subwatershed based on WatershedMVP and concentrations of dissolved inorganic nitrogen and orthophosphate. We also evaluated salinity as a measure of the extent of freshwater contributions at each site. We assessed correlations between metrics of CEC concentrations and each of these factors using the non-parametric Spearman (rho) correlation coefficients.

4. RESULTS

4.1. Wastewater compounds in sediments

We analyzed bed sediment samples for wastewater-related compounds using two USGS methods: 43 compounds were analyzed using Method SH5433 (Wastewater Compounds) and 20 compounds were analyzed using the Method SH6434 (Hormones). Of these 63 compounds, 11 were detected at least once, including five plant and animal biochemicals (PABs), two personal care and domestic use (PCDU) chemicals, one hormone, and three other compounds (Table 3).

PABs were detected in 30-100% of samples. Sources of PABs include sewage and natural organic material. The most frequently detected PABs were indole and cholesterol, although detection limits ranged by a factor of 10 among these compounds (50-500 μg/kg), which strongly influences detection frequencies. Skatole and indole are both fecal indicators and components of sewage.

Some PABs that were detected in other studies were not detected in our Cape Cod samples. For instance, in Phillips et al. (2016), 3β-coprostanol was detected in 92% of samples, with a median of 160 μg/kg, but was not detected in any of our samples above 50 μg/kg.

Among 17 hormones that were analyzed, estrone was the only hormone detected in Cape Cod sediment samples. Estrone, which is an endogenous estrogen that can end up in wastewater via excretion, was detected in sediment from Boat Meadow (0.79 μg/kg) and Quivett Creek (0.43 μg/kg). These two estuaries with low to moderate impacts septage based on indole and skatole sediment concentrations and November DIN concentrations. We did not measure total organic carbon (TOC) in our sediment samples, which may be an important consideration in explaining differences in which sites had the highest concentrations of specific wastewater related compounds.

Cape Cod samples showed lower levels and less frequent detections of hormones than coastal sediments in more urban areas. In Phillips et al. (2016), estrone was the second most frequently detected hormone (83%), with a median concentration of 0.57 μg/kg and a 90th percentile concentration of 1.9 μg/kg. The most frequently detected in Phillips et al. (2016), androstenedione, was not detected in any of our samples, and Phillips also detected seven other estrogen and androgen hormones that were not detected in our study. The lower detection frequencies and concentrations in the Cape Cod samples relative to the NY/NJ coastal samples may be related to less dense residential and commercial development and to loss of hormones through sorption during groundwater transport as sewage makes its way from septic systems through the aquifer into these tidal creeks. By contrast, the NY/NJ coastal systems were likely impacted by combined sewer overflows with untreated wastewater after Hurricane Sandy, as well as discharges from wastewater treatment plants.

4.2. Hormones in passive samplers

While estrone was the only hormone detected in sediment samples across all 10 sites, nine hormones—including estrone—were detected in POCIS passive samplers (Table 4). These included three androgens and nine estrogens. The most frequently detected hormones in the POCIS samplers were androstenedione, 17β-estradiol, and estrone, which all had 100% detection frequency. Androstenedione and estrone, along with progesterone, were the three most frequently detected hormones in Standley et al.'s (2008) study of hormones and pharmaceuticals in Cape Cod ponds.

The Rock Harbor site had the highest total hormone concentration and the highest number of detected hormones in the POCIS samplers; however, this sampler was covered in sand at the time of retrieval rather than remaining in the water column, so these results may be an artifact of the sampling rather than a true reflection of the presence of hormones in this creek. Total hormone concentrations and number of detected hormones were relatively similar across the other nine sites, with the highest concentrations found at the Boat Meadow, Old Harbor, and Sesuit Creek sites (Figure 2). While Quivett Creek was one of only two sites where estrone was detected in the sediments, the estrone concentration in the POCIS sampler from Quivett Creek had the lowest estone concentration, indicating that sites with the highest concentrations of hormones in sediments are not necessarily the sites with the highest water-phase concentrations.

4.3. PAHs in sediments

Polycyclic aromatic hydrocarbons (PAHs) were also measured using the wastewater method. All 10 PAHs on the analyte list were detected at least once (Table 5). Pyrene was detected in all sediment samples, and 3 PAHs were detected in nine of the 10 sediments (benzo[a]pyrene, fluoranthene, and phenanthrene). Scorton Creek had the highest total concentration of PAHs (2,915 μg/kg), and Scorton Creek and Old Harbor were the two sites at which all 10 PAHs were detected (Figure 2). The Pamet River sample also had relatively high total concentrations. Three sites did not have quantifiable concentrations of any PAHs: Namskaket Creek, Rock Harbor, and Sesuit Creek.

The highest total PAH concentration in the Scorton Creek samples was around half of the median sediment concentration (6,000 μg/kg) near a highly urbanized watershed in Phillips et al.'s (2016) study of NY and NJ coastal sediments. Total PAH concentrations in three additional Cape Cod samples were above the highest median concentration for five other watersheds in the same study by Phillips et al. (median concentrations ranged from <100 to 510 μg/kg). Four samples were within the range of median concentrations for these other NY and NJ watersheds.

The ratios of certain individual PAHs can indicate whether the primary source is pyrogenic (from combustion sources) or petrogenic (from unburned petroleum). One of these ratios is based on concentrations of fluoranthene (Fl) and pyrene (Pyr). According to studies cited by Phillips et al. (2016), the ratio of Fl/(Fl + Pyr) indicates primarily petroleum sources for values <0.4, petroleum combustion for values 0.4–0.5, and sewage or grass/wood/coal combustion for values >0.5. We were able to calculate this ratio for six of the 10 sediment samples and the resulting ratios ranged from 0.49 to 0.59, indicative of combustion of organic material rather than unburned petroleum, and primarily not from petroleum combustion. The other ratio is based on concentrations of anthracene (Ant) and phenanthrene (Phen). According to studies cited by Phillips et al. (2016), the ratio of Ant/(Ant + Phen) indicates primarily petroleum sources for values <0.1 and combustion sources for values >0.1. We were able to calculate this ratio for three samples, and the resulting values ranged from 0.20 to 0.25, which are also consistent with combustion sources.

Since our samples were collected in tidal creeks upstream of open water, the PAHs are less likely to have come from leakage or combustion of fuel used by boats, although there is substantial boat traffic in Pamet and Wellfleet Harbors that could influence the Pamet and Duck Creek sites. Additional sources may include runoff of fuel combustion by-products or burning of other organic material, potentially from automobiles, word-burning stoves or controlled/open burning. Phillips et al. (2016) observed higher Fl/(Fl + Pyr) values in less developed areas, suggesting that in these areas that combustion of other types of organic material, rather than petroleum sources, were relatively more important.

4.4. Pharmaceuticals in water

Water samples were analyzed for pharmaceuticals and other compounds using Method SH2440. Of the 109 compounds tested for, eight were detected in at least one sample (Table 6). Overall, the concentrations of detected pharmaceuticals ranged from 10 to 100 ng/L. Detection limits for pharmaceuticals ranged from 1 to 132 ng/L, so other compounds may have been present but not detectable with this method. Concentrations above 100 ng/L were observed for methotrexate and for select compounds detected at the Old Harbor site. Methotrexate was the most widely detected pharmaceutical, and had concentrations ranging from 40 to 180 ng/L. In other studies, methotrexate has not been frequently detected, and its widespread detection in these samples is unusual. Methotrexate is used to treat certain types of cancer of the breast, skin, head and neck, or lung. It is also used to treat severe psoriasis and rheumatoid arthritis. Its frequent detection in Cape Cod estuaries should be further investigated. After methotrexate, carbamazepine was the next most frequently detected, found at three sites. Carbamazepine is one of the most persistent pharmaceuticals, resistant to soil sorption and microbial degradation, and therefore more likely to persist in the environment. It was also one of the most frequently detected in the 2012 study of pharmaceuticals in Cape Cod Bay funded by MassBays (Costa 2012), and one of the most frequently detected CECs in SSI's studies of drinking water and ponds (Standley et al. 2008, Schaider et al. 2014, 2016). Lidocaine, caffeine and nicotine were each detected at two sites. These compounds, although not highly persistent, are ubiquitous in other studies of CECs in the environment and have a more constant input into the environment, maintaining what Daughton and Ternes (1999) characterize as pseudo-persistence.

Comparison data for coastal systems are not available for many of the pharmaceuticals that we detected in this study. Gaw et al. (2014) compiled concentrations of pharmaceuticals commonly detected in coastal systems globally, with maximum concentrations for individual compounds generally ranging from 100s to 1000s of ng/L. These maximum concentrations are higher than those found in this study and are expected in more urban areas with much higher input of wastewater discharges. Gaw et al.'s review also compiled information about ecotoxicity thresholds, with reported levels of concern for pharmaceuticals ranging from 250 to 30,000 ng/L. However, there are a growing number of ecotoxicology studies showing additional endpoints of concern such as changes in behavior that can alter survival. For instance, Brodin et al. (2013) showed that concentrations down to 1,800 ng/L of a psychiatric drug, oxazepam, affected activity, sociality, and feeding rates in perch. Furthermore, mixtures of pharmaceuticals may cause synergistic effects that are greater than anticipated from considering the toxicity of each compound individually.

4.5. PFASs in water

Of 16 PFASs that were analyzed in water samples and met laboratory QA/QC criteria, 12 were detected in at least one sample (Table 7). The most frequently detected PFASs, found in at least half of samples tested, included both long-chain (PFOA, PFNA, PFHxS, PFOS) and short-chain (PFHxA, PFHpA, PFBS) compounds. Most of the detected concentrations were between 0.1 and 1 ng/L. The compound with the highest maximum concentration was PFOS, which was detected at 10.2 ng/L (October) and 18.6 ng/L (September) at the Old Harbor site. The sites with the highest total PFAS concentrations (over 10 ng/L) were Old Harbor, Rock Harbor Pipe, and Namskaket. The other sites had total PFAS concentrations between 1 and 10 ng/L.

The Old Harbor site had the highest concentrations of PFOS and PFHxS (2.0 and 2.1 ng/L), while PFOA concentrations were more similar to other sites. The Old Harbor site had the highest levels for some pharmaceuticals, consistent with dense residential development served by septic systems. However, the relatively high concentrations of PFOS and PFHxS may be indicative of an additional source. Certain firefighting foams used to fight fuel fires, called aqueous film-forming foams (AFFFs), are responsible for groundwater and drinking water contamination close to military bases and airports across the U.S., and AFFF-impacted waters tend to be highest in PFOS and related compounds. On Cape Cod, sources of AFFF groundwater contamination include the Barnstable County Fire and Rescue Training Academy and Joint Base Cape Cod. These detections also may be consistent with a source related to the use of waterproof coatings used for shoes and upholstery. Future investigations should focus on potential sources in the area close to the Old Harbor site.

The relatively high PFAS concentrations at the Namskaket site may be related to wastewater discharges from the Tri-Town Septage Treatment Facility, which has a ground water discharge permit. This facility operated for about 25 years before being closed in 2016. Thorough work on the movement of the wastewater plume associated with this facility conducted by the USGS indicated that, based on nitrogen levels, the creek has not been impacted by the plume as of 2011 (Weiskel et al. 2016). However, five years have passed since the Weiskel et al. (2016) study, and the levels of PFAS detected at this site relative to other areas suggest that there is a source of contamination to the creek, indicating that further work may need to be conducted on the movement of this plume.

The high concentrations detected in the effluent from the Rock Harbor Pipe relative to the other sites could also be a result of the proximity of the wastewater facility of the Community of Jesus. In addition, groundwater discharge is a larger component of this creek than other sites included in this study. Whereas all other sites were tidal creeks, the Rock Harbor Pipe is a man-made structure designed to limit flooding of the Rock Harbor parking lot from the adjacent marsh system. Other water quality data (temperature, salinity, nitrate levels) support this observation. Therefore, while tidal flushing is a large factor in reducing levels of CECs at other sites, the Rock Harbor Pipe is not similarly influenced by tidal flushing.

In general, concentrations of total PFASs and individual PFASs were similar (within a factor of two) between September and October, with somewhat higher PFAS concentrations at the Old Harbor site in September and higher concentrations at Boat Creek and Pamet Creek in October (Figure 3). Analysis of the nutrient data from the September water samples collected from several of the sites showed lower than expected levels of nitrogen. For example, nitrate levels from the Rock Harbor Pipe effluent collected since 2013 averaged around 300 μM, but during September, these levels dropped to <3 μM. Salinity also increased from an average of 4 psu to nearly 20 psu. These observations indicate that groundwater was less of a contributor during September 2016 than any previous sampling event. The summer of 2016 was an unusually dry year, which likely affected groundwater flow. Although the Rock Harbor Pipe sample would be the most obviously impacted, other sites were also impacted. Additional nutrient sampling was conducted in October after the Cape had received several significant rainfall events and these results were more consistent with expected levels. Additional water samples for analysis of wastewater contaminants were collected in November 2016 but those results are not yet available.

We compared the concentrations of PFASs in our study with levels detected in a prior study of rural and urban coastal systems and freshwater systems in Rhode Island and the New York Metropolitan area (Zhang et al. 2016). For some PFASs at some sites in Cape Cod Bay estuaries, the levels of PFASs were consistent with the range of concentrations found in rural coastal systems. However, higher PFAS levels for some compounds at some Cape Cod sites were consistent with the concentrations in urban coastal systems, consistent with septic system impacts from densely developed areas served by septic systems, or potentially other sources of PFASs into groundwater associated with residential and commercial development. The concentrations of PFOS at the Old Harbor site were well above the maximum PFOS concentration in rural and coastal systems measured by Zhang et al. (1.9 ng/L), again consistent with an additional source beyond septic systems at this site.

4.6. PFASs in POCIS samplers

In general, PFASs were more frequently detected in POCIS samplers than in water samples (Table 8). The PFASs that were detected in at least half of water samples were all detected in at least 80% of the POCIS samplers. In addition, some PFASs that were not detected in water (FOSA, N-MeFOSAA) were detected in the POCIS samplers, which is consistent with our expectation that the passive samplers would be more sensitive to detecting compounds because they are deployed for a much longer period of time. While concentrations of PFASs in POCIS samplers were generally correlated with PFAS concentrations in water (Figure 5), we saw differences in the relative abundance of total PFASs across sites (Figure 3). For instance, total PFAS concentrations were highest in water samples from the Old Harbor site, while total PFAS concentrations were highest in the POCIS samplers from Namskaket. The data from by passive samplers complements the data from grab water samplers and provides a more complete assessment of both the range and relative abundances of compounds present in aquatic systems.

4.7. Predictors of CEC concentrations

We evaluated several metrics of septic system impact as predictors of CEC concentrations in Cape Cod tidal creeks (Table 9). We hypothesized that dissolved inorganic nitrogen (DIN) concentrations would be associated with CECs that primarily originate from septic systems. We considered both average DIN concentrations from 2016, which include summer months, and DIN concentrations from November 2016, when there is limited biological activity. DIN levels in summer months can be low even in creeks with high nitrogen loading due to uptake by primary producers, so fall DIN concentrations may better reflect N loading into these creeks. We observed that both measures of DIN were correlated with CEC concentrations in water, sediment, and POCIS samplers, although there were inconsistent patterns of whether the average DIN or November DIN concentrations were more strongly associated with metrics of CEC abundance. Total PFAS concentrations in water showed the strongest correlation with DIN, consistent with septic systems being the primary source of PFASs in Cape Cod groundwater (Figure 4). Total nitrogen loading, based on estimates from WatershedMVP modeling, was less strongly associated with CEC abundance than in-creek DIN measurements. This is not surprising, since overall nitrogen loading estimates do not account for proximity of sources to the receiving water body, and the watershed areas delineated in WatershedMVP may not correspond to the area contributing to creek water at our sampling locations. November 2016 orthophosphate concentrations were less strongly correlated with metrics of CEC abundance than DIN concentrations.

We also hypothesized that we would observe inverse associations between salinity and CEC concentrations in water, since we anticipated that groundwater (freshwater) inputs would be the main source of CECs. Although water samples were all collected at low tide, we still saw salinity concentrations that covered the range from freshwater to seawater conditions, with the highest salinities measured in September with groundwater inputs were particularly low. Salinity showed a strong inverse association with PFAS concentrations (Figure 4), but surprisingly showed a weak positive association with total pharmaceutical concentrations. However, the total pharmaceutical concentrations were based on a limited number of detected compounds, particularly because the detection limits were relatively high, so the total pharmaceutical concentration we measured may not be a good indicator of overall inputs of pharmaceuticals and other CECs from septic systems.

5. CONCLUSIONS

This study is the most comprehensive assessment of contaminants of emerging concern, including pharmaceuticals, personal care products, and highly fluorinated compounds (PFASs) in estuaries in Cape Cod Bay. We found that CECs were commonly detected in tidal creeks impacted by septic systems. PFASs were more commonly detected than pharmaceuticals, although this may reflect in part lower detection limits that provided greater analytical sensitivity. PFAS concentrations at some sites were higher than those associated with rural coastal systems in other regions. Elevated PFOS concentrations at the Old Harbor site in Sandwich may be indicative of an additional, non-wastewater source. While the concentrations measured in this study are below ecotoxicological thresholds that have been identified thus far, the presence of mixtures of these xenobiotic compounds do raise concerns about potential ecotoxicological effects.

We found associations between dissolved inorganic nitrogen concentrations and the presence of CECs. This finding reinforces prior associations between nitrate concentrations and CECs in Cape

Cod drinking water wells and ponds. As Cape Cod communities develop wastewater management plans to address nutrient pollution in surface water bodies, it is important to consider the presence of CECs in nutrient-rich groundwater and the potential for CEC bioaccumulation and ecological impacts in areas most affected by septic system pollution.

Building on the findings of this study, future work will further refine our land use analyses to more accurately delineate the areas that are most likely to contribute to the water quality at our sampling locations. We anticipate receiving additional data on pharmaceuticals in water samples collected later in 2016 when these creeks likely received greater contributions from groundwater inputs. Finally, we plan to conduct additional sampling in the Old Harbor/Dock Creek area to determine whether there is a non-wastewater source contributing to elevated PFOS levels at this site.

6. OUTREACH AND DISSEMINATION OF STUDY FINDINGS

Preliminary findings from this study were presented at the New England Water Environment Association Spring Meeting in Falmouth (June 2017), at Silent Spring Institute's annual research update in Hyannis (October 2017), and at the Cohasset Center for Student Coastal Research (November 2017).

We plan to submit the findings from this study for publication in a peer-reviewed journal such as *Environmental Science & Technology*. Publication of this paper will be accompanied by a press release, media outreach, and content for social media in order to disseminate key study findings broadly.

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Table 1. Ten Cape Cod Bay embayments sampled in this study. The area of the watershed used in the calculations is the land area only. GIS data for N loading, septic wastewater flow, number of parcels, and watershed area were provided by the Cape Cod Commission. Dissolved inorganic nitrogen (DIN) data presented in the table are an average of samples taken every two weeks, May–November 2016.

Locations are listed in increasing distance from Cape Cod Canal.

Embayment	Watershed	Subwatershed	N load (kg/year /km^2)	WW flow (gallons /day /km^2)	Parcels (/km^2)	2016 average DIN (µM)	Latitude	Longitude
Sandwich Harbor	Sandwich Harbor	Dock Creek LT10	1134	31261	247	67.9	41.758	-70.489
Scorton Creek	Scorton Harbor	Scorton Creek LT10	645	18388	115	7.3	41.731	-70.406
Sesuit Creek/ Sesuit Harbor	Sesuit Harbor	Sesuit Creek West LT10	1691	46630	278	9.3	41.745	-70.163
Quivett Creek	Quivett Creek	Quivett Creek	791	21807	164	13.4	41.754	-70.131
Namskaket Creek/Little Namskaket Creek	Namskaket	Namskaket Stream	635	17521	149	28.6	41.781	-70.011
Namskaket Creek/Little Namskaket Creek	Little Namskaket	Little Namskaket	795	21920	183	26.6	41.791	-70.01
Boat Meadow Creek/Rock Harbor	Rock Harbor	Cedar Pond	1483	40884	186	14.3	41.797	-69.992
Boat Meadow Creek/Rock Harbor	Boat Meadow	Boat Meadow River	1110	30621	227	13.6	41.807	-69.996
Wellfleet Harbor	Wellfleet Harbor	Duck Creek LT10	1969	54292	266	35.8	41.934	-70.027
Pamet River/Little Pamet River	Pamet River	Pamet River	346	9546	87	13.7	41.994	-70.05

Table 2. Dates in 2016 of deployment and retrieval of passive samplers and collection of sediment and water samples.

Embayment	SubWatershed	WQ Monitoring Station	POCIS Deployed	PE Sampler Deployed	Sediment Samples	Water Samples (PPCPs)	Water Samples (PFAS)		POCIS and PE Sampler Retrieved
Sandwich Harbor	Dock Creek LT10	Old Harbor-Dewey	16-Aug	31-Aug	31-Aug	31-Aug	31-Aug	13-Oct	13-Oct
Scorton Creek	Scorton Creek LT10	Scorton Creek - Jones Ln	16-Aug	31-Aug	31-Aug	31-Aug	31-Aug	13-Oct	13-Oct
Sesuit Creek/Sesuit Harbor	Sesuit Creek West LT10	Sesuit Creek	16-Aug	3-Sep	3-Sep	3-Sep	3-Sep	13-Oct	13-Oct
Quivett Creek	Quivett Creek	Quivett Marsh	16-Aug	3-Sep	3-Sep	3-Sep	3-Sep	13-Oct	13-Oct
Namskaket Creek/Little Namskaket Creek	Namskaket Stream	Upper Namskaket	15-Aug	3-Sep	3-Sep	3-Sep	3-Sep	12-Oct	12-Oct
Namskaket Creek/Little Namskaket Creek	Little Namskaket	Little Namskaket Creek	14-Aug	1-Sep	1-Sep	1-Sep	1-Sep	12-Oct	12-Oct
Boat Meadow Creek/Rock Harbor	Cedar Pond	RH-culvert	15-Aug	2-Sep	2-Sep	2-Sep	2-Sep	12-Oct	12-Oct
Boat Meadow Creek/Rock Harbor	Boat Meadow River	Inner Boat Meadow	15-Aug	1-Sep	1-Sep	1-Sep	1-Sep	12-Oct	12-Oct
Wellfleet Harbor	Duck Creek LT10	Duck Creek	17-Aug	2-Sep	2-Sep	2-Sep	2-Sep	12-Oct	12-Oct
Pamet River/Little Pamet River	Pamet River	Pamet River	17-Aug	2-Sep	2-Sep	2-Sep	2-Sep	12-Oct	12-Oct

Table 3. Concentrations of 11 wastewater compounds detected in bed sediment samples in 10 Cape Cod tidal creeks, 2016. nd = not detected. dnq = detected but not quantified. Concentrations in micrograms per kilogram (µg/kg).
PAB: Plant and animal biochemical, PAH: Polycyclic aromatic hydrocarbon, PCDU: Personal care/Domestic use

	β-Sitosterol (PAB)	β-Stigmastanol (PAB)	Cholesterol (PAB)	Indole (PAB)	Skatole (PAB)	Estrone (hormone)	4-Cumylphenol (PCDU)	d-Limonene (PCDU)	Bis(2-ethyl hexyl) phthalate (other)	Carbazole (Other)	p-Cresol (Other)	Sum of concentrations	Number detected
Cape Cod estuaries													
Boat Meadow	2,110	nd	1,502	144	dnq	0.793	nd	dnq	nd	nd	1,450	5,207	7
Duck	nd	nd	935	dnq	nd	nd	127	nd	nd	dnq	nd	1,062	4
Little Namskaket	nd	nd	1,420	136	dnq	nd	nd	dnq	nd	nd	dnq	1,556	5
Namskaket	3,560	1,330	207	271	dnq	nd	nd	dnq	nd	nd	dnq	5,368	7
Old Harbor	4,050	1,050	2,506	283	dnq	nd	nd	nd	nd	dnq	dnq	7,889	7
Pamet	4,880	900	5,994	463	dnq	nd	nd	nd	nd	dnq	dnq	12,237	7
Quivett	nd	nd	nd	dnq	nd	0.434	nd	dnq	nd	dnq	nd	0.434	4
Rock Harbor	nd	nd	724	dnq	nd	nd	nd	nd	dnq	nd	nd	724	3
Scorton	nd	nd	1,697	122	dnq	nd	nd	nd	nd	dnq	nd	1,819	4
Sesuit	nd	nd	803	dnq	nd	nd	nd	dnq	nd	nd	nd	803	3
Summary statistics													
Detection frequency (%)	40	30	90	100	60	20	10	50	10	50	50		
Maximum concentration	4,880	1,330	5,994	463	dnq	0.793	127	dnq	dnq	dnq	1450		
Detection limit	500	500	120	100	50	0.25	50	50	250	50	250		
Comparison data from 6 coastal systems in New York and New Jersey (Phillips et al. 2016)													
Median	590	nd	2,000	120	10	0.57							
75th percentile	1,100	700	3,300	330	31	1.04							
90th percentile	2,700	1,200	5,300	650	57	1.9							

Table 4. Hormones and plant/animal biochemicals extracted (ng/sampler) from POCIS samplers deployed in 10 Cape Cod tidal creeks, August – October 2016.

	Androstenedione (androgen)	**Epitestosterone (androgen)**	**Testosterone (androgen)**	**17-alpha-Estradiol (estrogen)**	**17-beta-Estradiol (estrogen)**	**Estriol (estrogen)**	**Estrone (estrogen)**	**Equilenin (estrogen)**	**Equilin (estrogen)**	**Cholesterol (PAB)**	**Sum of hormone masses detected (ng/sampler)**	**Number of detected hormones**
Cape Cod estuaries												
Boat Meadow	4.66	<0.5	<0.4	0.271	1.85	<0.5	9.26	2.09	<4	241	18.1	5
Duck	2.58	<0.5	<.4	<0.2	0.91	<0.5	3.75	<0.71	<4	368	7.25	3
Little Namskaket	3.03	<0.5	<0.4	<0.2	0.72	<0.5	4.13	<0.5	<4	274	7.88	3
Namskaket	2.85	<0.5	<0.4	<0.2	0.58	<0.5	4.57	<0.5	<4	233	8.00	3
Old Harbor	2.90	<0.5	0.849	<0.2	1.79	<0.5	6.05	1.80	<4	580	13.4	5
Pamet	3.58	<1.89	<.4	<0.2	0.80	<0.5	5.10	<0.5	<4	154	9.47	3
Quivett	2.32	<0.5	<.4	<0.2	0.45	<0.5	2.59	<0.876	<4	479	5.36	3
Rock Harbor	4.81	0.708	<0.4	3.54	32.3	0.494	99.0	8.96	28.9	727	179	8
Scorton	3.50	<0.5	<.4	<0.2	0.677	<0.5	3.17	<0.5	<4	862	7.34	3
Sesuit	2.66	<0.5	<.4	0.287	1.62	<0.5	6.89	<0.5	<4	2,549	11.5	4
Summary statistics												
Detection frequency (%)	100	10	10	30	100	10	100	30	10	100		
Maximum concentration	4.81	0.71	0.85	3.54	32.3	0.49	99.0	8.96	28.9	2,549		
Detection limit	0.5	0.5	0.4	0.2	0.4	0.5	0.5	0.5	4	100		

Table 5. Concentrations of 10 PAHs detected in bed sediment samples in 10 Cape Cod tidal creeks, 2016.

PAH measurements conducted with USGS Method 5433, Wastewater compounds in sediments.
nd = not detected. dnq = detected but not quantified. Concentrations in micrograms per kilogram (µg/kg).

	1-Methyl-naphthalene	**2-Methyl-naphthalene**	**2,6-Dimethyl-naphthalene**	**Anthracene**	**Anthraquinone**	**Benzo[a]pyrene**	**Fluoranthene**	**Naphthalene**	**Phenanthrene**	**Pyrene**	**Sum of PAH concentrations**	**Number detected**
Cape Cod estuaries												
Boat Meadow	nd	nd	dnq	nd	dnq	dnq	51.5	nd	dnq	dnq	52	6
Duck	dnq	nd	dnq	dnq	dnq	102	303	nd	188	216	809	8
Little Namskaket	nd	nd	dnq	dnq	dnq	dnq	69	nd	dnq	73.1	142	7
Namskaket	nd	nd	dnq	nd	dnq	dnq	dnq	nd	dnq	dnq	0	6
Old Harbor	dnq	dnq	dnq	50.5	56.4	149	380	dnq	176	277	1,089	10
Pamet	nd	nd	105	59.5	60.2	292	558	nd	179	384	1,638	7
Quivett	nd	nd	nd	dnq	nd	dnq	117	nd	92.9	89.9	300	5
Rock Harbor	nd	nd	nd	nd	nd	dnq	dnq	nd	dnq	dnq	0	4
Scorton	dnq	dnq	dnq	131	110	299	1020	dnq	534	821	2,915	10
Sesuit	nd	nd	dnq	nd	nd	nd	nd	nd	nd	dnq	0	2
Summary statistics												
Detection frequency (%)	30	20	80	60	70	90	90	20	90	100		
Maximum concentration	dnq	dnq	105	131	110	299	1,020	dnq	534	821		
Detection limit	50	50	50	50	50	50	50	50	50	50		
Comparison data from 6 coastal systems in New York and New Jersey (Phillips et al. 2016)												
Median	nd	nd	34	18	27	29	84	nd	32	71		
75th percentile	23	72	87	150	120	240	470	78	210	480		
90th percentile	74	160	160	330	190	550	1,500	270	810	1,700		

Table 6. Concentrations of pharmaceuticals in water samples from 10 Cape Cod Bay tidal creeks, September 2016. (a) Prescription drugs. Pharmaceutical measurements conducted with USGS Method 2440, Pharmaceutical compounds in water.
nd = not detected. dnq = detected but not quantified. Concentrations in nanograms per liter (ng/L).

	Carbamazepine	**Desvenlafaxine**	**Lidocaine**	**Meprobamate**	**Metformin**	**Methotrexate**	**Theophylline**	**Venlafaxine**
Cape Cod estuaries								
Boat Meadow	nd	nd	nd	nd	nd	72.2	nd	nd
Duck	nd	nd	nd	nd	nd	179	nd	nd
Little Namskaket	nd	nd	nd	nd	nd	43.5	nd	nd
Namskaket	nd	nd	nd	nd	nd	nd	nd	nd
Old Harbor	dnq	dnq	dnq	nd	17	71.6	100	12
Pamet	nd	nd	nd	nd	nd	46.6	nd	nd
Quivett	nd	nd	nd	nd	28	101	nd	nd
Rock Harbor	nd	nd	dnq	dnq	nd	nd	nd	nd
Scorton	nd	nd	nd	nd	nd	nd	nd	nd
Sesuit	dnq	nd	nd	nd	nd	nd	nd	nd
Summary statistics								
Detection frequency (%)	18	9	18	9	18	55	9	9
Maximum concentration	dnq	dnq	dnq	dnq	27.9	179	100	12.1
Detection limit	2.2	42	19	17	6.6	26	40	2.6

Table 6 (cont'd). (b) Non-prescription drugs, total pharmaceutical concentrations (prescription and non-prescription), and number of pharmaceuticals detected.

	1,7-Dimethyl-xanthine	Acetaminophen	Caffeine	Cotinine	Nicotine	Sum of pharmaceutical concentrations	Number detected
Cape Cod estuaries							
Boat Meadow	nd	nd	nd	nd	nd	72	1
Duck	nd	nd	nd	4.5	31.6	215	3
Little Namskaket	nd	nd	nd	nd	nd	43	1
Namskaket	nd	nd	nd	nd	nd	0	0
Old Harbor	459	35.7	984	nd	40.5	1719	11
Pamet	nd	nd	nd	nd	nd	47	1
Quivett	nd	nd	nd	nd	nd	128	2
Rock Harbor	nd	nd	nd	nd	nd	0	2
Scorton	nd	nd	nd	nd	nd	0	0
Sesuit	nd	nd	nd	nd	nd	0	1
Summary statistics							
Detection frequency (%)	9	9	9	9	18		
Maximum concentration	459	35.7	984	4.5	40.5		
Detection limit	9	9	9	9	18		

Table 7. PFAS concentrations in water samples collected from 10 Cape Cod tidal creeks, 2016.
(a) Concentrations of sulfonate- and sulfonamide-containing PFASs.

		PFBS	PFHxS	PFOS	N-EtFOSAA	6:2 FtS
Cape Cod estuaries						
Boat Meadow	Sept.	nd	0.124	nd	nd	nd
	Oct.	0.295	0.220	0.442	nd	nd
Duck	Sept.	nd	0.180	nd	nd	nd
Little Namskaket	Sept.	0.293	0.255	0.615	nd	nd
	Oct.	0.505	0.305	0.421	nd	0.221
Namskaket	Sept.	0.522	0.609	0.665	nd	nd
	Oct.	0.555	0.626	0.910	nd	nd
Old Harbor	Sept.	0.928	2.026	18.606	0.215	nd
	Oct.	1.289	2.079	10.236	nd	nd
Pamet	Sept.	nd	0.106	nd	nd	nd
	Oct.	0.183	0.230	0.724	nd	nd
Quivett	Sept.	nd	0.085	nd	nd	nd
	Oct.	0.134	0.100	0.433	nd	nd
Rock Harbor	Sept.	nd	0.287	0.401	nd	nd
	Oct.	0.291	0.153	0.509	nd	nd
Rock Harbor Pipe	Sept.	3.718	1.377	1.299	0.282	0.371
Scorton	Sept.	0.303	0.303	nd	nd	nd
Sesuit	Sept.	0.466	0.281	nd	nd	nd
	Oct.	0.568	0.230	0.355	nd	nd
Summary statistics						
Detection frequency (%)		74	100	68	11	11
Maximum concentration		3.72	2.08	18.61	0.28	0.37
Detection limit		0.02	0.068	0.319	0.17	0.22
Coastal and freshwater systems in Rhode Island and the New York Metropolitan Area (Zhang et al. 2016)						
Rural coastal systems ($N = 4$)		0.13 - 0.28	<0.06 - 0.34	0.16 - 0.63	<0.012 - 0.058	0.004 - 0.022
Urban coastal systems ($N = 5$)		<0.08 - 1.2	0.41 - 5.1	0.74 - 1.9	0.031 - 0.065	0.008 - 0.46
Freshwater systems ($N = 28$)		<0.08 - 6.2	<0.06 - 35	<0.05 - 23.2	<0.012 - 0.94	<0.07 - 15.3

Table 7 (cont'd). b). Concentrations of carboxylic acid PFASs, total PFAS concentrations, and number of PFASs detected.

		PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	Sum all PFASs	# detected (of 16)
Cape Cod estuaries									
Boat Meadow	Sept.	0.433	0.545	nd	0.390	0.182	nd	1.67	5
	Oct.	0.770	0.922	1.489	0.622	0.401	0.257	5.42	9
Duck	Sept.	0.360	0.461	nd	0.449	0.308	0.252	2.01	6
Little Namskaket	Sept.	0.521	0.657	1.438	0.563	0.244	nd	4.59	8
	Oct.	0.856	0.725	1.409	0.456	0.204	nd	4.88	8
Namskaket	Sept.	2.713	1.043	3.606	nd	nd	nd	9.16	6
	Oct.	2.349	1.216	4.685	0.664	0.185	0.191	11.4	9
Old Harbor	Sept.	1.609	0.719	1.563	0.246	nd	nd	25.9	8
	Oct.	1.830	0.685	1.270	nd	nd	nd	17.4	6
Pamet	Sept.	nd	nd	nd	0.352	0.153	nd	0.61	3
	Oct.	1.402	0.736	0.928	0.382	nd	nd	4.58	7
Quivett	Sept.	0.420	0.449	nd	0.420	0.226	nd	1.51	4
	Oct.	0.968	nd	nd	nd	nd	nd	1.63	4
Rock Harbor	Sept.	0.745	0.854	1.589	0.745	0.462	0.356	5.44	8
	Oct.	0.655	0.812	1.252	0.532	0.268	0.157	4.63	9
Rock Harbor Pipe	Sept.	6.606	3.799	4.871	0.380	0.353	nd	23.1	10
Scorton	Sept.	0.439	0.443	nd	0.391	0.201	nd	2.08	6
Sesuit	Sept.	1.476	0.353	nd	nd	nd	nd	2.57	4
	Oct.	0.804	nd	nd	nd	nd	nd	1.96	4
Summary statistics									
Detection frequency (%)		95	84	58	74	63	26		
Maximum concentration		6.61	3.80	4.87	0.75	0.46	0.36		
Detection limit		0.22	0.26	0.80	0.23	0.12	0.11		
Coastal and freshwater systems in Rhode Island and the New York Metropolitan Area (Zhang et al. 2016)									
Rural coastal systems (*N* = 4)		<0.29 - 1.2	<0.62 - 0.9	0.27 - 1.3	0.074 - 0.4	0.038 - 0.17	<0.02 - 0.097		
Urban coastal systems (*N* = 5)		1.56 - 3.5	1.6 - 3.2	1.97 - 7	0.31 - 0.6	0.13 - 0.3	<0.02 - 0.097		
Freshwater systems (*N* = 28)		<0.29 - 48.4	<0.62 - 48.2	0.59 - 47.3	0.1 - 14	<0.03 - 5.8	<0.02 - 1.9		

Table 8. PFASs extracted (ng/sampler) from POCIS samplers deployed in 10 Cape Cod tidal creeks, August-October 2016.
(a) Concentrations of sulfonate- and sulfonamide-containing PFASs.

	PFBS	PFHxS	PFOS	FOSA	N-MeFOSAA	N-EtFOSAA	6:2 FtS
Cape Cod estuaries							
Boat Meadow	1.308	1.452	7.131	0.051	0.098	0.113	0.066
Duck	1.036	1.318	4.728	0.021	nd	0.133	nd
Little Namskaket	0.935	5.154	2.944	0.009	nd	0.045	0.054
Namskaket	1.340	8.044	13.080	0.044	0.075	0.161	nd
Old Harbor	4.002	19.544	16.467	0.035	nd	0.414	0.333
Pamet	0.648	2.079	7.210	0.025	nd	0.051	nd
Quivett	nd	0.897	3.071	0.038	0.044	0.079	nd
Rock Harbor	nd	4.384	11.566	0.059	nd	0.102	0.044
Scorton	1.235	4.523	9.797	0.019	nd	nd	0.050
Sesuit	0.999	2.194	4.127	0.021	0.054	0.027	nd
Summary statistics							
Detection frequency (%)	80	100	100	100	40	90	50
Maximum concentration	4.0	19.5	16.5	0.06	0.10	0.41	0.33
Detection limit	0.158	0.036	0.025	0.004	0.022	0.014	0.043

Table 7 (cont'd). (b) Masses of extracted carboxylic acid PFASs, total PFAS concentrations, and number of PFASs detected.

	PFHxA	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUnA**	**PFDoDA**	**Sum all PFASs**	**# detected (of 14)**
Cape Cod estuaries									
Boat Meadow	1.403	4.799	9.447	3.802	1.280	0.586	0.112	31.65	14
Duck	2.466	3.490	6.778	2.334	0.695	0.265	nd	23.26	11
Little Namskaket	2.076	3.308	9.070	1.928	0.526	0.153	nd	26.20	12
Namskaket	6.873	10.765	61.612	4.795	1.283	0.506	0.138	108.72	13
Old Harbor	8.924	7.387	15.627	2.542	0.536	0.124	0.049	75.98	13
Pamet	1.183	4.391	10.220	4.435	1.261	0.333	0.038	31.87	12
Quivett	2.452	3.477	5.657	2.257	0.635	0.186	nd	18.79	11
Rock Harbor	1.948	6.795	19.629	5.339	2.617	0.691	0.065	53.24	12
Scorton	3.042	4.965	9.293	3.341	0.798	0.234	nd	37.30	11
Sesuit	3.509	3.780	7.837	2.439	0.560	0.182	0.044	25.77	13
Summary statistics									
Detection frequency (%)	100	100	100	100	100	100	60		
Maximum concentration	8.92	10.76	61.61	5.34	2.62	0.69	0.14		
Detection limit	0.403	0.413	0.415	0.126	0.098	0.046	0.037		

Table 9. Spearman rho correlation coefficients among predictors of CECs and metrics of detected CECs in 10 Cape Cod tidal creeks. Coefficients in **bold** correspond to $p<0.05$.

	Estimated septic system N loading	**Dissolved inorganic N 2016 average**	**Dissolved inorganic N November 2016**	**Orthophosphate November 2016**	**Salinity**
Sum wastewater compounds in sediment	-0.503	0.333	0.212	-0.018	-0.624
Number of wastewater compounds in sediment	-0.581	0.366	0.038	0.013	-0.290
Sum of hormones in POCIS samplers	0.236	0.115	**0.685**	0.467	-0.164
Sum of PAHs in sediment	-0.325	-0.043	-0.387	-0.313	-0.215
Number of PAHs in sediment	-0.190	0.355	-0.012	0.006	-0.532
Sum of pharmaceuticals in water	0.219	0.475	-0.231	0.044	0.219
Number of pharmaceuticals in water	0.397	0.472	0.000	0.384	0.094
Sum of PFASs in water	0.152	0.612	**0.794**	0.721	**-0.709**
Number of PFASs in water	0.218	0.536	0.467	0.374	-0.436
Sum of PFASs in POCIS samplers	-0.333	0.333	**0.673**	0.576	**-0.806**

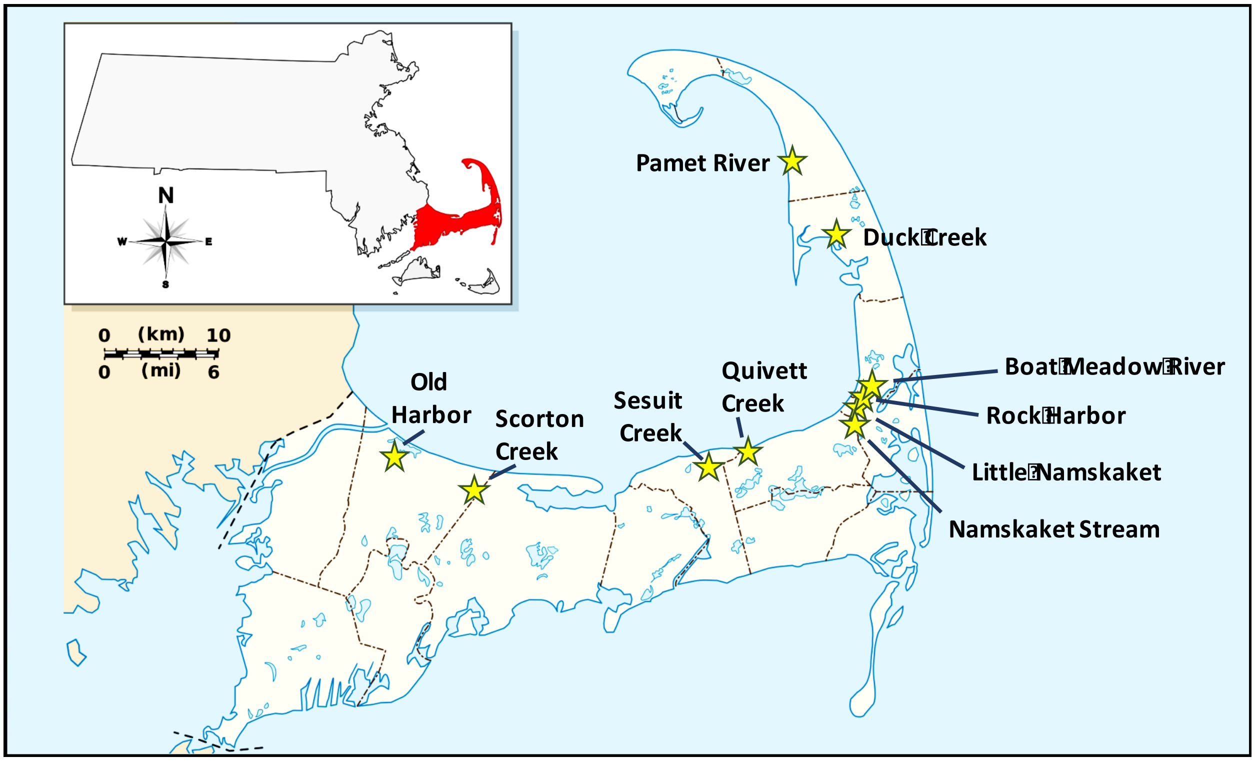
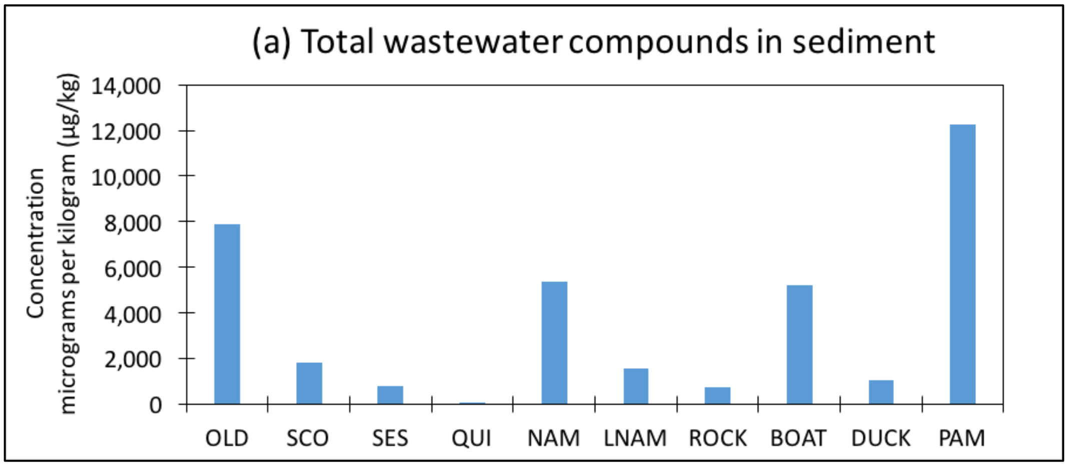
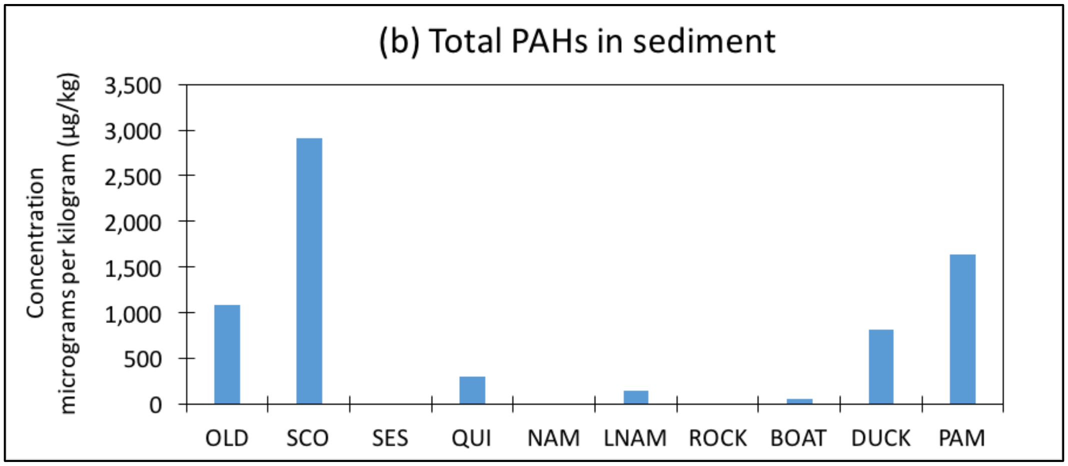


Figure 1. Map of field collection sites in Cape Cod Bay tidal creeks.





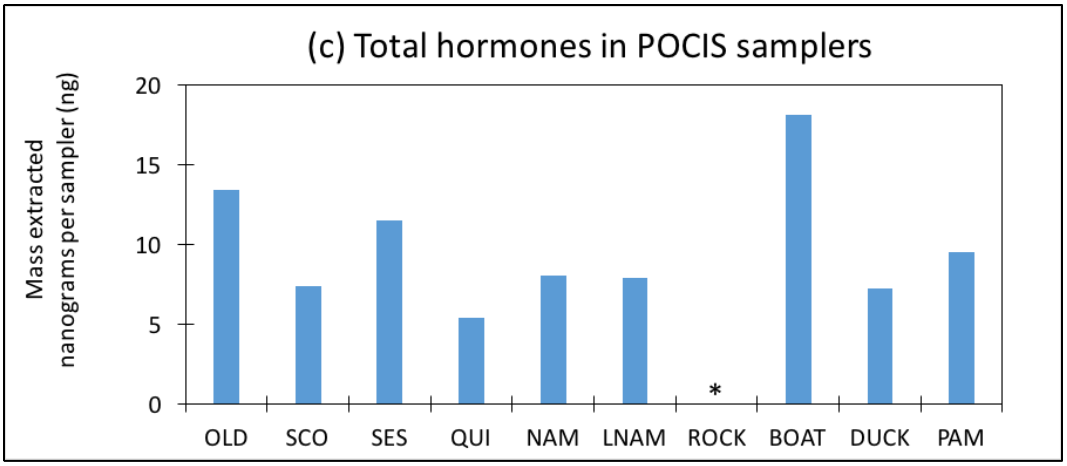
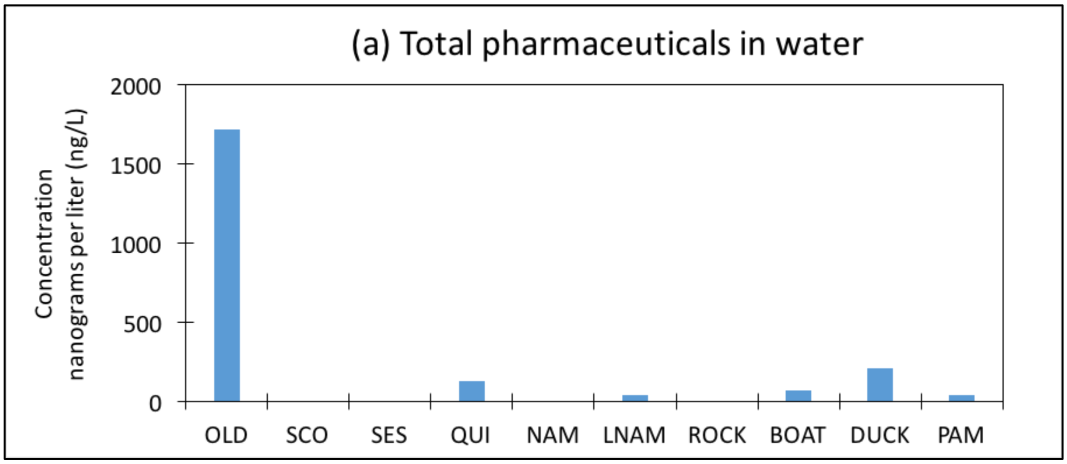
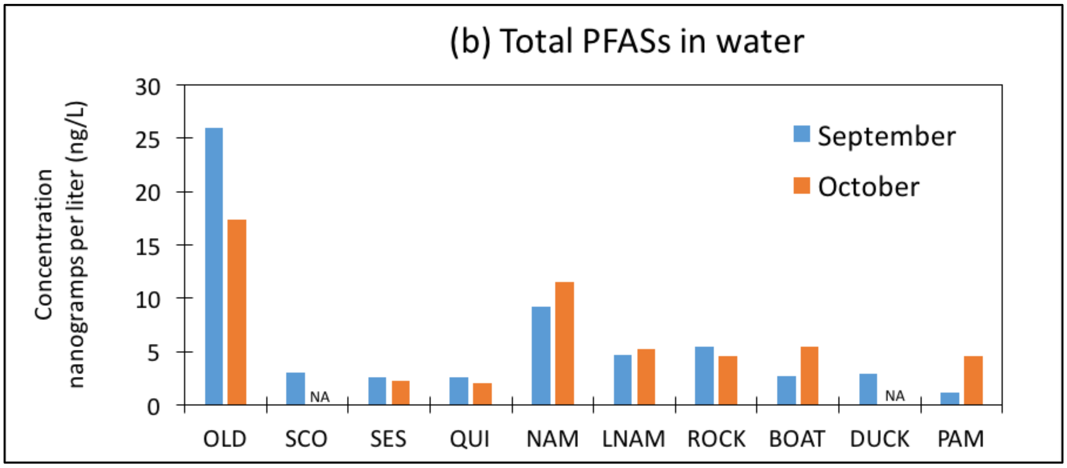


Figure 2. Sediment concentrations of (a) wastewater-related compounds and (b) PAHs in sediments from 10 Cape Cod Bay tidal creek collected in September 2016 and (c) concentrations of hormones extracted from POCIS samplers deployed August–October 2016. Sites are sorted from the Upper Cape (closest to the Cape Cod Canal) on the left to the Outer Cape (closest to the tip of Cape Cod) on the right. *POCIS sampler from Rock Harbor site covered in sand so results are not considered reliable.





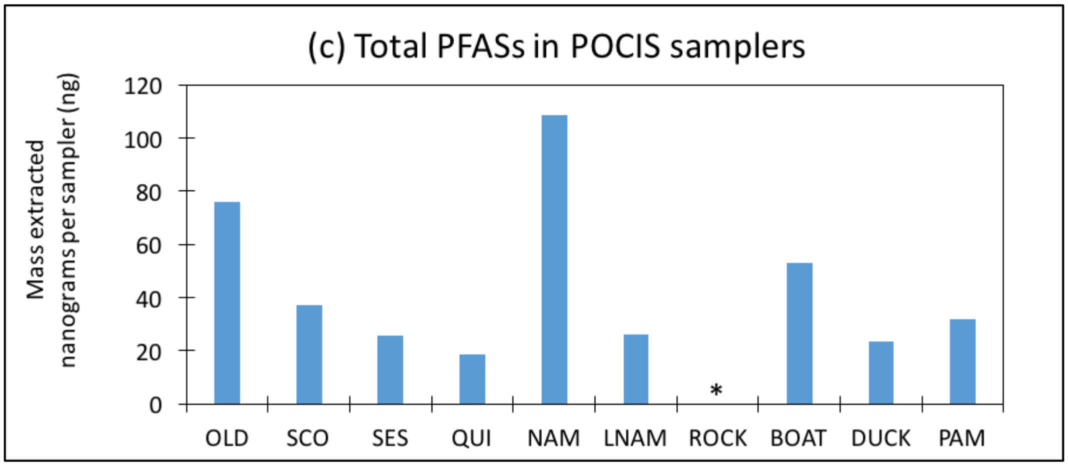


Figure 3. Total concentrations of (a) pharmaceuticals and (b) PFASs in water samples collected from 10 Cape Cod Bay tidal creeks in September and October 2016. Pharmaceutical concentrations are only available for September. Sites are sorted from the Upper Cape (closest to the Cape Cod Canal) on the left to the Outer Cape (closest to the tip of Cape Cod) on the right. Water samples were only analyzed for pharmaceuticals in September, and were not analyzed from Scorton and Duck Creeks in October. *POCIS sampler from Rock Harbor site covered in sand so results are not considered reliable.

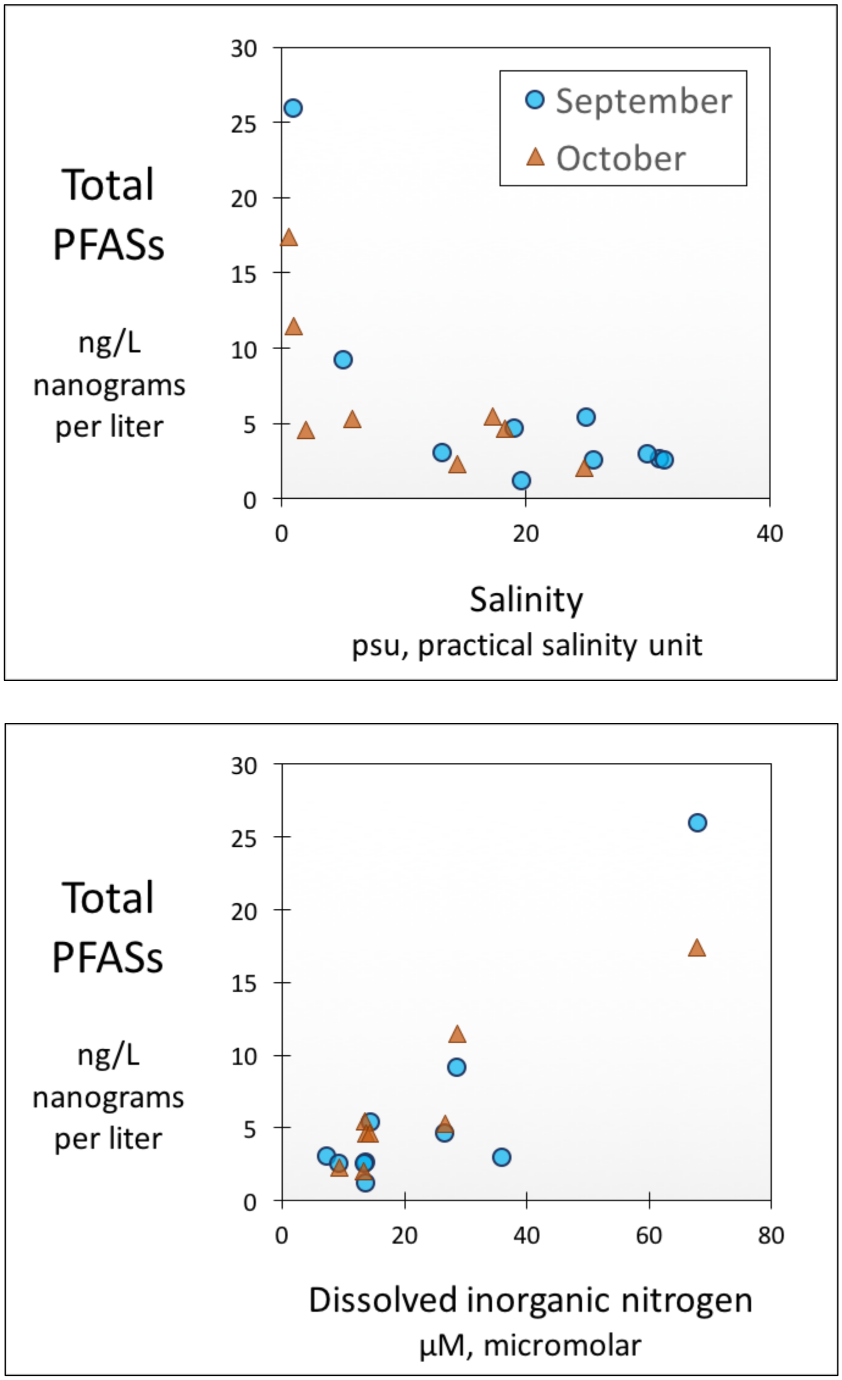


Figure 4. Associations between total PFAS concentrations and (a) salinity and (b) 2016 dissolved inorganic nitrogen concentrations in September (blue circles) and October (orange triangles) 2016.

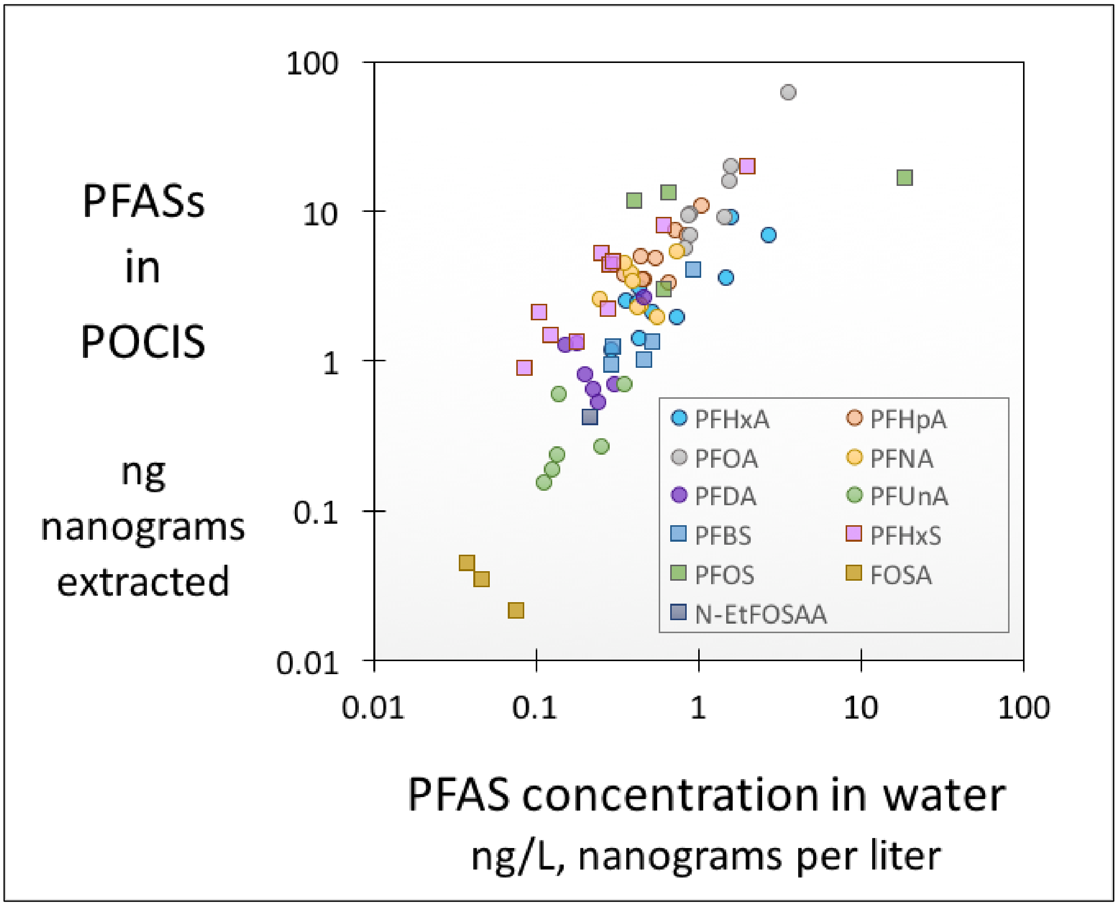


Figure 5. Associations between PFAS concentrations in September 2016 water samples and August to October POCIS samplers.

Appendix A. Complete list of target analytes.
PAB: Plant and animal biochemical
PAH: Polycyclic aromatic hydrocarbon
PCDU: Personal care / Domestic use
PPCP: Pharmaceuticals and personal care products

Compound	Compound Group	Method Detection Limit	Reporting Limit	Detected?
Wastewater compounds in sediment (Method SH5433). Concentrations in micrograms per kilogram (μg/kg)				
1,4-Dichlorobenzene	PCDU	50	100	
4-Cumylphenol	PCDU	50	100	Yes
4-n-Octylphenol	PCDU	50	100	
4-Nonylphenol (sum of all isomers)	PCDU	750	1500	
4-Nonylphenol diethoxylate (NP2EO), all isomers	PCDU	1000	2000	
4-Nonylphenol monoethoxylate (NP1EO), all isomers	PCDU	500	1000	
4-tert-Octylphenol	PCDU	50	100	
4-tert-Octylphenol diethoxylate (OP2EO)	PCDU	50	100	
4-tert-Octylphenol monoethoxylate (OP1EO)	PCDU	250	500	
Acetophenone	PCDU	150	300	
Benzophenone	PCDU	50	100	
Camphor	PCDU	50	100	
d-Limonene	PCDU	50	100	Yes
Galaxolide (HHCB)	PCDU	50	100	
Isoborneol	PCDU	50	100	
Isoquinoline	PCDU	100	200	
Menthol	PCDU	50	100	
N,N-diethyl-meta-toluamide (DEET)	PCDU	100	200	
Phenol	PCDU	50	100	
Tonalide (AHTN)	PCDU	50	100	
Triclosan	PCDU	50	100	
Atrazine	Pesticide	100	200	
Bromacil	Pesticide	500	1000	
Chlorpyrifos	Pesticide	50	100	
Diazinon	Pesticide	50	100	
Metolachlor	Pesticide	50	100	
Prometon	Pesticide	50	100	
3-Methyl-1(H)-indole (Skatole)	PAB	50	100	Yes
β-Sitosterol	PAB	500	1000	Yes
β-Stigmastanol	PAB	500	1000	Yes
Indole	PAB	100	200	Yes
Diethyl phthalate	Plasticizer	100	200	
Tributyl phosphate	Plasticizer	50	100	
Triphenyl phosphate	Plasticizer	50	100	
Tris(2-butoxyethyl)phosphate	Plasticizer	150	300	
Tris(2-chloroethyl)phosphate	Plasticizer	100	200	
Tris(dichloroisopropyl)phosphate	Plasticizer	100	200	
1-Methylnaphthalene	PAH	50	100	Yes
2,6-Dimethylnaphthalene	PAH	50	100	Yes
2-Methylnaphthalene	PAH	50	100	Yes
Anthracene	PAH	50	100	Yes

Anthraquinone	PAH	50	100	Yes
Benzo[a]pyrene	PAH	50	100	Yes
Fluoranthene	PAH	50	100	Yes
Naphthalene	PAH	50	100	Yes
Phenanthrene	PAH	50	100	Yes
Pyrene	PAH	50	100	Yes
2,2',4,4'-Tetrabromodiphenylether (PBDE 47)	Other	50	100	
3-tert-Butyl-4-hydroxy anisole (BHA)	Other	150	300	
Bis(2-ethylhexyl) phthalate	Other	250	500	Yes
Carbazole	Other	50	100	Yes
Isophorone	Other	50	100	
Isopropylbenzene	Other	100	200	
p-Cresol	Other	250	500	Yes
Hormones in sediment (Method SH6434). Concentrations in micrograms per kilogram (μg/kg)				
17β-Estradiol	Estrogen	0.2	0.4	
11-ketotestosterone	Androgen	na	0.52	
4-Androstene-3,17-dione	Androgen	0.25	0.5	
cis-Androsterone	Androgen	0.25	0.5	
Dihydrotestosterone	Androgen	0.5	1	
Epitestosterone	Androgen	0.5	1	
Testosterone	Androgen	0.2	0.4	
17a-Ethynylestradiol	Estrogen	0.1	0.2	
17a-Estradiol	Estrogen	0.1	0.2	
Equilin	Estrogen	2	4	
Equilenin	Estrogen	0.26	0.52	
Estriol	Estrogen	0.26	0.52	
Estrone	Estrogen	0.25	0.5	Yes
Mestranol	Estrogen	0.2	0.4	
trans-diethylstilbestrol	Estrogen	na	0.33	
Norethindrone	Progestin	0.2	0.4	
Progesterone	Progestin	1.5	3	
3β-coprostanol	PAB	na	50	
Cholesterol	PAB	na	120	Yes
Bisphenol A	PCDU	na	20	
Pharmaceuticals in water (Method SH2440). Concentrations in nanograms per liter (ng/L)				
10-Hydroxy-amitriptyline	Antidepressant	1.7	8.3	
Amitriptyline	Antidepressant	19	37	
Bupropion	Antidepressant	3.6	18	
Citalopram	Antidepressant	3.3	6.6	
Desvenlafaxine	Antidepressant	42	84	Yes
Duloxetine	Antidepressant	7.3	37	
Fluoxetine	Antidepressant	5.4	27	
Fluvoxamine	Antidepressant	27	80	
Norfluoxetine	Antidepressant	40	80	
Norsertraline	Antidepressant	40	80	
Norverapamil	Antidepressant	4.3	8.6	
Paroxetine	Antidepressant	132	264	
Sertraline	Antidepressant	3.2	16	
Venlafaxine	Antidepressant	2.6	5.2	Yes
Chlorpheniramine	Antihistamine	27	54	
Diphenhydramine	Antihistamine	9.5	19	
Fexofenadine	Antihistamine	48	96	
Hydroxyzine	Antihistamine	1.5	7.4	

Loratadine	Antihistamine	1.4	7	
Promethazine	Antihistamine	20	80	
Abacavir	Antiviral	4.1	8.2	
Acyclovir	Antiviral	4.4	22	
Lamivudine	Antiviral	3.2	16	
Nevirapine	Antiviral	145	290	
Oseltamivir	Antiviral	2.9	15	
Penciclovir	Antiviral	40	80	
Valacyclovir	Antiviral	33	163	
Atenolol	Beta-Blocker/Heart	4.8	13	
Clonidine	Beta-Blocker/Heart	30	61	
Dehydronifedipine	Beta-Blocker/Heart	15	30	
Desmethyldiltiazem	Beta-Blocker/Heart	35	70	
Diltiazem	Beta-Blocker/Heart	5.1	10	
Ezetimibe	Beta-Blocker/Heart	80	205	
Fenofibrate	Beta-Blocker/Heart	7.1	14	
Metoprolol	Beta-Blocker/Heart	14	27	
Nadalol	Beta-Blocker/Heart	10	20	
Pentoxifylline	Beta-Blocker/Heart	4.7	9.4	
Propranolol	Beta-Blocker/Heart	13	26	
Verapamil	Beta-Blocker/Heart	70	140	
Cimetidine	Diabetic/Ulcer/Antacid	21	42	
Famotidine	Diabetic/Ulcer/Antacid	17	34	
Glipizide	Diabetic/Ulcer/Antacid	40	80	
Glyburide	Diabetic/Ulcer/Antacid	29	58	
Metformin	Diabetic/Ulcer/Antacid	6.6	13	Yes
Nizatidine	Diabetic/Ulcer/Antacid	40	80	
Omeprazole + Esomprazole	Diabetic/Ulcer/Antacid	8.2	16	
Ranitidine	Diabetic/Ulcer/Antacid	96	192	
Sitagliptin*	Diabetic/Ulcer/Antacid	19	97	
Codeine	Opiate	44	88	
Hydrocodone	Opiate	3.5	10	
Loperamide	Opiate	40	80	
Methadone	Opiate	3.8	7.6	
Morphine	Opiate	20	80	
Oxycodone	Opiate	5	25	
Propoxyphene	Opiate	3.4	17	
Tramadol	Opiate	7.5	15	
Amphetamine	Stimulant/Abuse	4.1	8.1	
Dextromethorphan	Stimulant/Abuse	1.6	8.2	
Diazepam (valium)	Stimulant/Abuse	2	4	
Lorazepam	Stimulant/Abuse	101	202	
Oxazepam	Stimulant/Abuse	113	226	
Pseudoephedrine + Ephedrine	Stimulant/Abuse	5.5	11	
Temazepam	Stimulant/Abuse	9.2	18	
Acetaminophen	Pain reliever	10	20	Yes
Albuterol	Pharm-Other	1.2	6.7	
Alprazolam	Pharm-Other	6.6	21	
Antipyrine	Pharm-Other	58	116	
Benztropine	Pharm-Other	22	44	
Betamethasone	Pharm-Other	57	114	
Carbamazepine	Anticonvulsant	2.2	11	Yes
Carisoprodol	Pharm-Other	25	50	
Erythromycin	Pharm-Other	27	80	
Fadrozole	Pharm-Other	6.3	13	

Fluconazole	Pharm-Other	35	71	
Fluticasone propionate	Pharm-Other	0.92	4.6	
Hydrocortisone	Pharm-Other	73	147	
Iminostilbene	Pharm-Other	73	145	
Ketoconazole	Pharm-Other	56	113	
Lidocaine	Anesthetic	19	38	Yes
Meprobamate	Antianxiety	17	86	Yes
Metaxalone	Pharm-Other	7.8	16	
Methocarbamol	Pharm-Oth	5.6	11	
Methotrexate	Cancer treatment	26	52	Yes
Nordiazepam	Pharm-Other	10	20	
Phenazopyridine	Pharm-Other	4.1	13	
Phendimetrazine	Pharm-Other	16	31	
Phenytoin	Pharm-Other	94	188	
Prednisolone	Pharm-Other	75	150	
Prednisone	Pharm-Other	84	168	
Quinine	Pharm-Other	16	80	
Raloxifene	Pharm-Other	40	80	
Sulfadimethoxine	Pharm-Other	33	65	
Sulfamethizole	Pharm-Other	21	104	
Sulfamethoxazole*	Pharm-Oth	13	26	
Tamoxifen	Pharm-Other	na	270	
Theophylline	Respiratory disease	40	80	Yes
Thiabendazole	Pharm-Other	5.4	11	
Tiotropium	Pharm-Other	100	200	
Triamterene	Pharm-Other	2.6	5.2	
Trimethoprim	Pharm-Other	5.8	19	
Warfarin	Pharm-Other	3	6	
1,7-Dimethylxanthine (p-Xanthine)	Caffeine/Nicotine	21	88	Yes
Caffeine	Caffeine/Nicotine	43	91	Yes
Cotinine	Caffeine/Nicotine	1.7	6.4	Yes
Nicotine	Caffeine/Nicotine	29	58	Yes
methyl-1H-benzotriazole	Other	28	80	
Piperonyl butoxide	Other	10	20	
Atrazine	PEST	9.7	19	
PFASs in water. Concentrations in nanograms per liter (ng/L)				
PFHxA	PFAS	0.44		Yes
PFHpA	PFAS	0.22		Yes
PFOA	PFAS	0.80		Yes
PFNA	PFAS	0.23		Yes
PFDA	PFAS	0.18		Yes
PFUnDA	PFAS	0.11		Yes
PFDoDA	PFAS	0.26		
PFBS	PFAS	0.05		Yes
PFHxS	PFAS	0.07		Yes
PFOS	PFAS	0.32		Yes
PFDS	PFAS	0.15		
6:2 FtS	PFAS	0.22		Yes
8:2 FtS	PFAS	0.10		Yes
N-MeFOSAA	PFAS	0.12		
N-EtFOSAA	PFAS	0.17		Yes
FOSA	PFAS	0.04		