

Exploratory Study of Emerging Contaminants in Select Florida Rivers

**Division of Environmental Assessment and Restoration
Florida Department of Environmental Protection**

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Executive Summary

The Florida Department of Environmental Protection (DEP) performed a study to evaluate sampling techniques and technologies, analytical methods, and toxicological assays of emerging contaminants (EC) in Florida's fresh waters. The study used varying types of sample collection devices and analytical methods, applying a small-scale study design. Seventy-five surface water Trend Network monitoring sites were sampled monthly during 2012 and 2015 by the Division of Environmental Assessment and Restoration (DEAR) for wastewater tracers, including sucralose. Four of these river sites—in the Apalachicola, Withlacoochee, Ochlockonee, and Alafia Rivers—were selected for this study based on the sucralose results.

Polar organic compound integrative samplers (POCIS) and semi-permeable membrane devices (SPMD) were deployed at each river site in March 2017. One-time whole water grab samples were taken when the devices were retrieved 30 to 35 days later. SGS AXYS Laboratories and the DEP Laboratory conducted chemical analyses. These focused on 6 categories of EC: pesticides, pharmaceuticals and personal care products (PPCPs) perfluorinated compounds (PFCs), polybrominated diphenyl ethers (PBDEs), alkylphenols, and hormones. The University of Florida (UF) and U.S. Geological Survey (USGS) conducted biological evaluations. POCIS and SPMD extracts and whole water samples from each site were screened using *in vitro* receptor assays.

Outcomes

- Sampling and chemical analyses for EC are sensitive processes, in part because of the low laboratory detection limits, commonly less than 10 nanograms per liter, used to determine the presence of these compounds. Because of this, chemical analyses are accompanied by lengthy quality control (QC) reports that must be carefully reviewed to determine data usability.
- For the passive sampling devices, time-weighted averages of analyte concentrations are sufficient for determining biological exposure rates. To determine time-weighted average concentrations for passive sampling devices, the sampling rates (uptake rate of compound onto passive sampling material adjusted for flow dynamics) of individual compounds should be determined. Furthermore, performance reference compounds (PRCs) should be deployed with the passive samplers so that site-specific uptake distributions can be determined for individual compounds.
- For test protocols that measure estrogenicity and androgenicity, the high level of color in Florida waters caused interference in detections. An increased understanding of site-specific sampling rates for estrogenic and androgenic compounds and further refinement of the laboratory methods used for the determination of estrogenicity and androgenicity are recommended for future studies.
- Future studies of EC in Florida's waterbodies should focus on waterbodies directly affected by known sources of these substances (e.g., river segments continually impacted by wastewater overflows). This approach would reduce the burden of collecting and processing data by focusing on known contaminant sources.

1.0 Introduction

In 2008, a Florida Department of Environmental Protection (DEP) internal workgroup assessed the efficacy of sample collection techniques to determine the bioavailability and occurrence of categories of compounds, commonly referred to as emerging contaminants (EC). These substances, which have been detected in low concentrations in surface waters throughout the U.S. and abroad, include chemicals found in pharmaceuticals and personal care products, flame retardants, pesticides and their degradates, fragrances and flavorants, detergent degradates, plasticizers, solvents, and polycyclic aromatic hydrocarbons (Kolpin et al. 2002; Pal et al. 2010). Several of these compounds are known mutagens and endocrine disruptors; however, most of them are unregulated (Chemical Abstracts Service [CAS] 2013).

The DEP workgroup reconvened in 2013 to evaluate how it could respond to the growing problem. It recommended carrying out a study to investigate the likely causes of biological effects by employing screening assays to detect ecological effects, such as estrogenic activity, occurring in Florida's waters.

By 2016, the workgroup had developed a study design that was deployed in 2017. Site selection for the study was based on the detection frequency of a known wastewater tracer compound (sucralose) from monthly sampling conducted at 78 statewide surface water Trend Network sites in 2012 and 2015. The main objective of the study was to evaluate novel sampling techniques and technologies, analytical methods, and toxicological assays for EC in Florida rivers. The study used varying types of sample collection devices and analytical methods to address the objective, applying a small-scale study design. A wide range of compounds were evaluated because of the ubiquitous nature of EC.

1.1 Historical Context

Monitoring for chemical tracers in the environment is a powerful tool for characterizing anthropogenic pollutants and identifying potential pollutant sources (i.e., point and nonpoint sources). Sucralose (trade name Splenda) is an effective compound to use as a tracer because it is present in domestic wastewater discharge at detectable levels, does not occur naturally, has low toxicity, is highly soluble in water, is ineffectively metabolized and removed by wastewater treatment processes, and persists in the environment (Labare and Alexander 1993; Oppenheimer et al. 2011; Soh et al. 2011; Tollefsen et al. 2012). DEP's monitoring of sucralose has helped to identify sites for intensive study and to track contaminant migration routes in surface water and groundwater.

To better understand the extent of Florida's freshwater resources potentially affected by EC, DEP's Division of Environmental Assessment and Restoration (DEAR) began to collect and analyze samples for wastewater tracers and imidacloprid in its Status and Trend Monitoring Networks (DEP 2015). DEAR sampled statewide for sucralose in both networks in 2012 (Seal et al. 2016), and for sucralose, the pharmaceuticals acetaminophen, carbamazepine, and primidone, and the neonicotinoid pesticide imidacloprid in both networks in 2015 (Silvanima et al. 2018). All these compounds are hydrophilic and therefore may be highly mobile in the freshwater environment (Bonmatin et al. 2015; Jenner and Smithson 1989; Wishart et al. 2006).

Sucralose was commonly detected at ultra-trace levels, with a laboratory method detection limit (MDL) of 0.01 micrograms per liter ($\mu\text{g/L}$) in the Status and Trend Networks in 2012 and 2015. Sucralose was found in all freshwater resources monitored: rivers, streams, canals, lakes, and both unconfined and confined aquifers. Statewide Status Network sucralose detection frequencies for combined water resources were 43.3 % (2012) and 55.3 % (2015). Status Network sampling in 2015 provided statewide ultra-trace detection frequencies of 16.5 % for the occurrence of any of the pharmaceuticals, and 39.4 % for imidacloprid. Of the water resources sampled, rivers consistently produced the highest detection frequencies. Statewide monthly Trend Network sampling of 75 rivers, streams, and canals revealed sucralose detection frequencies of 77.3 % (2012) and 86.7 % (2015) at the sites sampled. Twenty-eight of these sites had detection frequencies greater than 80 % for the combined 24-month period.

2.0 Study Design

2.1 Site Selection

Of the 75 trend stations sampled (**Figure 1**), the 4 containing the most frequent sucralose detections, as determined by using only values greater than the method detection and practical quantification limits of DEP's instrumentation, were selected for this study.

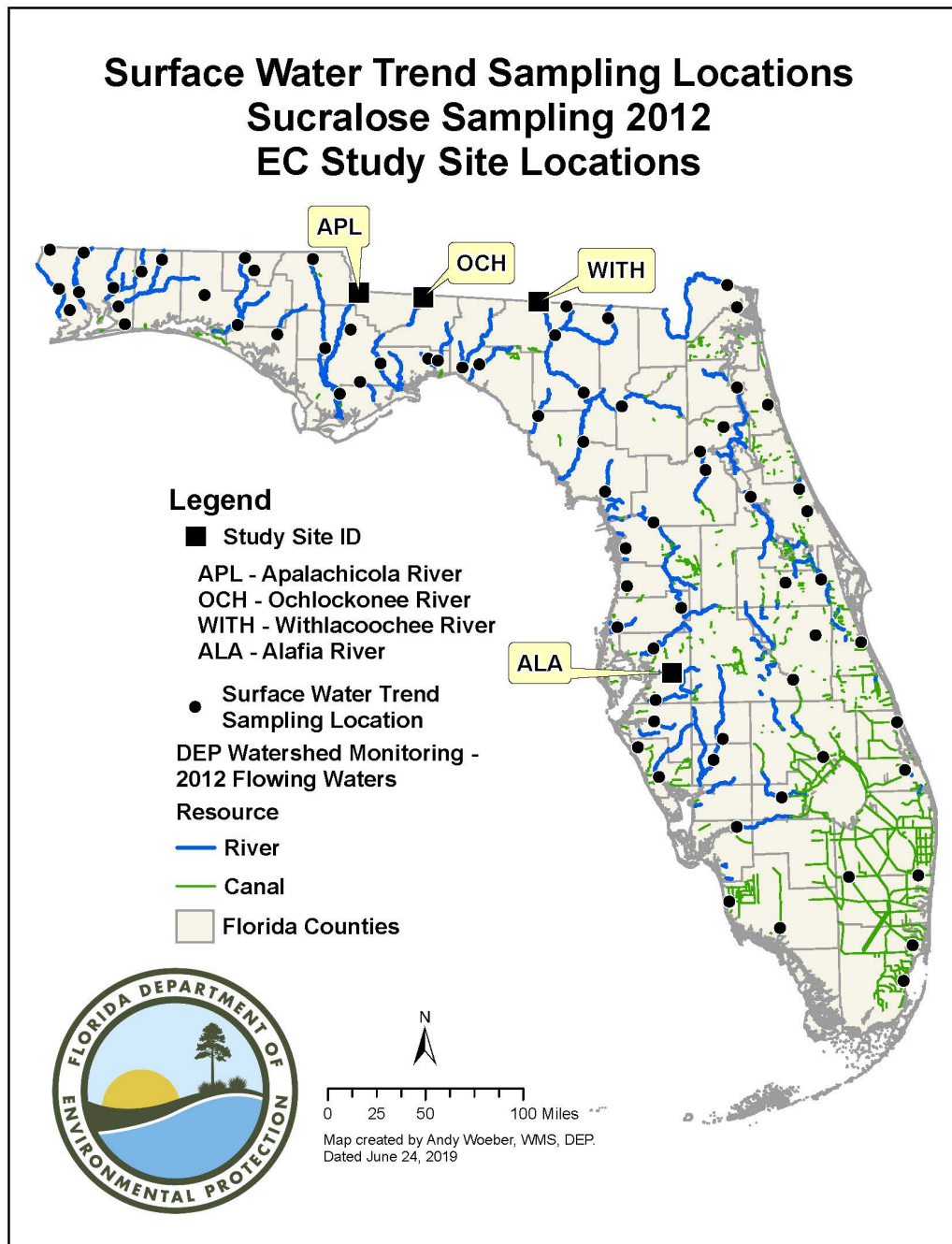


Figure 1. Surface water Trend Network sites selected for study

2.2 Site Characterization

The 4 sites chosen for the study were rivers, each with at least a 15-year history of regular monthly sampling by DEP staff for a suite of standard water quality analytes (e.g., nutrients, major ions). Three of the rivers—the Apalachicola, the Withlacoochee and the Ochlockonee—flow into Florida from Georgia over the Atlantic Coastal Plain province. The watersheds of the Ochlockonee and Withlacoochee Rivers each have significant amounts of agricultural and silvicultural activity. The Apalachicola River, formed by the confluence of the Flint and the Chattahoochee Rivers near Albany, Georgia, drains much of that state. It is used for sanitary waste disposal by millions of people in many cities, including metropolitan Atlanta, Griffin, Columbus, and Bainbridge. The Chattahoochee River has three federally maintained water control structures (dams) upstream, which slow flow and pool the river. This provides an opportunity for sedimentation to occur before the water is released farther downstream. The fourth site is located on the Alafia River, which flows west into Tampa Bay from the center of the Florida peninsula, with its headwaters near the City of Lakeland.

2.3 Sampling Techniques

The greatest number of EC detections is expected when using a combination of sampling methods, such as polar organic chemical integrative samplers (POCIS), semipermeable membrane devices (SPMD), and whole water grab samples (Alvarez 2010). The passive samplers (POCIS and SPMD) are used for long-term deployment (30 to 35 days), while the grab sample technique is used to capture a discrete snapshot in time. Some types of chemicals are found in both sampling devices. However, the SPMD is selected for neutral organic chemicals, such as polybrominated diphenyl ethers (PBDEs), and the POCIS is selected for more water-soluble organic chemicals, such as hormones (Alvarez 2010).

For this study, POCIS, SPMD, and grab samples were used at each site. Three POCIS and three SPMD contained in one large canister (**Figure 2**) were deployed at each river site for the study in March 2017. Grab samples were collected when the devices were retrieved 30 to 35 days later. A field blank for each sampling method (POCIS, SPMD, and grab) was collected at the Apalachicola River site.

2.4 EC Categories

EC are categorized based on their manufacturing or commercial use. Each category of EC compounds tends to have similar exposure routes, aquatic life effects, and chemical characteristics (**Table 1**).

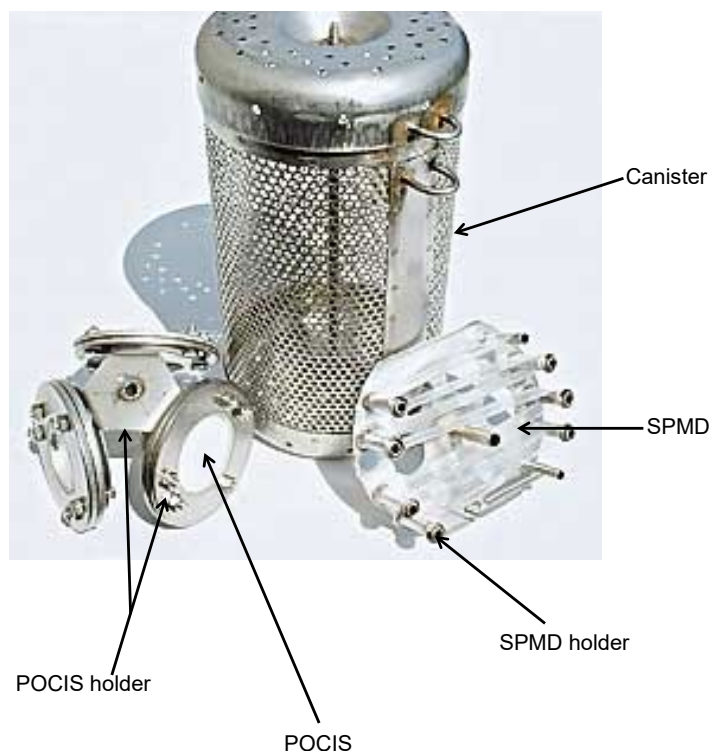


Figure 2. Diagram of the POCIS and POCIS holder, SPMD and SPMD holder, and a large canister to contain the passive samplers

Table 1. General categories of EC (adapted from Dellinger et al. 2011)

Category	Primary Routes of Potential Human Exposure	Aquatic Life Effects	Polarity/ Water Solubility
Pesticides	Dermal contact; ingestion (e.g., contaminated food or water); inhalation (e.g., breathing vapors, dust, or spray particles); ocular exposure	Toxic, potential endocrine disruptor (ED)	Most are polar and have high solubility
PPCPs	Ingestion (e.g., oral medications); inhalation (e.g., aerosol hair products, perfumes); dermal contact (e.g., topical medications, deodorants, lotions)	ED	Most are polar and have high solubility
Synthetic Hormones	Ingestion (e.g., contaminated food or water, oral medications); inhalation (e.g., dust and particulates); dermal contact	ED	Polar/high solubility
PFCs	Ingestion (e.g., contaminated food or water, breast milk); hand-to-mouth from surfaces that contain PFCs	Bioaccumulative, ED	Polar/high solubility
PBDEs	Ingestion (e.g., contaminated food, water, breast milk); inhalation; dermal contact	Toxic, bioaccumulative, ED, carcinogenic	Nonpolar/ low solubility
Alkylphenols	Ingestion (contaminated food or water); contact with some personal care products and detergents; inhalation (primarily indoor air, dusts)	ED	Range of polarities/ generally low solubility

2.5 Overview of Laboratory Analysis

2.5.1 Chemical

The group of laboratory analyses performed was determined based on the type of sampling device (**Table 2**). Not all analytes were analyzed for each sample type. The analytes were targeted based on the range of organic contaminants most appropriate for each sampling device. The SGS AXYS Lab and DEP Lab conducted the analyses.

2.5.2 Biological

Several EC, such as pesticides and hormones, are known to be estrogenic and androgenic in rivers, meaning that they can cause reproductive changes in fish and wildlife (U.S. Geological Survey [USGS] 2019). EC may also cause genotoxic effects (DNA damage) to aquatic life. Biological response tests were used to measure endocrine activity in cell lines exposed to samples. The University of Florida (UF) and USGS conducted the biological screening. POCIS dialysis, SPMD extracts, and whole water from each site were screened using the *in vitro* receptor assays listed in **Table 3**.

3.0 Results

Table 2 lists the chemistry results for the study by EC category and by analytical laboratory. Qualitative results are used so that comparisons can be made between sampling types (see the discussion in **Section 4.0**). All compound categories were detected at all sites in at least one sampling type. **Table 3** lists the biology categories by test type and laboratory. **Appendix B** lists detected analytes.

Table 2. Number of compounds analyzed in each category

* The DEP Lab used a reduced analyte list for some sampling devices. POCIS samples were not analyzed for 29 pesticide compounds. SPMD samples were not analyzed for 1 pesticide compound.

**SPMD samples were not analyzed for PPCPs by the SGS AXYS Lab.

N/A = Not applicable

Category	Sampling Devices Used	Number of Compounds Analyzed by SGS AXYS Lab	Number of Compounds Analyzed by DEP Lab
Pesticides	POCIS, SPMD, and Grab	76	88*
PPCPs	POCIS, SPMD,** and Grab	127	4
Hormones	POCIS and Grab	17	N/A
PFCs	POCIS and Grab	13	N/A
PBDEs	SPMD and Grab	8	N/A
Alkylphenols	SPMD and Grab	4	N/A

Table 3. Assay categories with assay name and entity conducting assay

Assay Category	Assay Name	Entity Conducting Assay
Receptor Binding Assay	Estrogen and androgen receptor binding by fluorescence polarization	UF
Receptor Transactivation Assay	Estrogen and androgen transactivation assay by using both agonist and antagonist modes	UF
Receptor Binding Assay	Bioluminescent yeast estrogen and androgen screens (BLYES and BLYAS)	USGS
Genotoxicity Assay	SOS Chromotest	USGS

3.1 Pesticides – SGS AXYS Lab

Analysis was performed on all samples for 76 pesticide compounds, 42 of which were detected at 1 or more stations, in at least 1 sample type (SPMD, POCIS, or grab samples). Of the 42 compounds detected, 41 were found using a combination of SPMD and grab samples. Thirty-one compounds were detected at all stations ($N = 4$). Detections for 18 compounds were qualified because of lab or field blank detections.

3.2 PPCPs – SGS AXYS Lab

Analysis was performed on POCIS and grab samples for 127 PPCP compounds; 39 were detected at 1 or more stations, in at least 1 sample type. Of the 39 compounds detected, 31 compounds were found in POCIS samples and 24 compounds were found in grab samples. Seven compounds were detected at all stations ($N = 4$). Detections for 3 compounds were qualified because of lab or field blank detections.

3.3 Hormones – SGS AXYS Lab

Analysis was performed on POCIS and grab samples for 17 hormone compounds; 5 compounds were detected at 1 or more stations, in at least 1 sample type. All compounds detected were found in the POCIS samples, and 2 of the compounds detected were found only in grab samples. One compound was detected at all stations ($N = 4$). All grab sample detections were qualified because of lab or field blank detections, but no data from POCIS samples were qualified for this reason.

3.4 PFC – SGS AXYS Lab

Analysis was performed on POCIS and grab samples for 13 PFC compounds; 10 compounds were detected at 1 or more stations, in at least 1 sample type. Eight of the compounds detected were found in the POCIS samples, and 7 of the compounds detected were found in grab samples. Three compounds were detected at all stations ($N = 4$). No PFC data were qualified because of lab or field blank detections.

3.5 PBDEs – SGS AXYS Lab

Analysis was performed on SPMD and grab samples for 8 PBDE compounds, all of which were detected by both sampling types at 1 or more sites. For SPMD, all compounds were found at all sites, while 4 of the 8 were detected at all sites for grab. All SPMD detections and 92 % of grab detections were qualified because of lab or field blank detections.

3.6 Alkylphenols – SGS AXYS Lab

Analysis was performed on SPMD and grab samples for 4 alkylphenol compounds; 2 compounds were detected at all sites (N=4), in at least 1 sample type. Both compounds detected were found in the SPMD samples, but only 1 was found in the grab samples. All alkylphenol data were qualified because of lab or field blank detections.

3.7 Pesticides and PPCPs – DEP Lab

Grab samples were analyzed for all 92 compounds (88 pesticides and 4 PPCPs), SPMDs were analyzed for 91 compounds (87 pesticides and 4 PPCPs), and POCIS were analyzed for 63 compounds (59 pesticides and 4 PPCPs). Thirty-two compounds (29 pesticides and 3 PPCPs) were detected at 1 or more stations, in at least 1 sample type. Fourteen compounds were detected at all stations (N = 4). No data from this laboratory were qualified because of lab or field blank detections.

3.8 UF Results

UF conducted bioanalytical assays (receptor binding and transactivation) on whole water grab samples and extracts from the SPMD and POCIS samplers. For the receptor binding assays, interference from background fluorescence was an issue when analyzing the whole water grab and POCIS extract samples. This interference was likely because of the naturally high total organic carbon (TOC) and humic acids in the water present at the study sites. These preclude any conclusions from being drawn concerning the presence or absence of estrogenic or androgenic compounds in POCIS and grab samples.

However, background fluorescence did not cause notable interference in the interpretation of the binding assay results for the SPMD extracts. For these extracts, on a qualitative basis, there was a positive indication of estrogen receptor and androgen receptor binding chemicals at each of the study sites. The transactivation assays also yielded variable results most likely because of interference. Further analysis of additional river sites and the use of additional sample clean-up steps for dark-water rivers are needed before conclusions about the presence or absence and effects of estrogenic or androgenic compounds can be drawn with confidence.

3.9 USGS Results

USGS used the SOS Chromotest to test each of the sample types (POCIS, SPMD, grab) at each river site and on a field blank. All sites were negative for genotoxicity in all sample types, except at the Alafia River site, where the POCIS and SPMD samples tested positive.

USGS also tested samples at all sites and from all sample types using BLYES and BLYAS. The grab samples from the Alafia, Apalachicola, and Withlacoochee River sites were found to be estrogenic. POCIS samples were found to be estrogenic at all sites, while SPMD samples were not estrogenic at any site. No androgenic activity was found in any sample type or at any site.

4.0 Lessons Learned and Recommendations

Sampling and chemical analyses for EC is a sensitive process, as evidenced by the frequent detections in QC samples (field and lab blanks). Chemical analyses are accompanied by lengthy QC reports that must be carefully reviewed when determining the use of the data. Selecting sampling and analysis methods based on the goals and objectives of the study would reduce the burden of collecting and processing data in future studies.

A comparison of the concentrations obtained using the three sampling techniques was not possible because of the difference in measurement units between the passive devices and grab samples. This was in part because sampling rates for these compounds were not determined. Alvarez (2010) defines sampling rate as the rate in liters per day (L/d) of water extracted by the passive sampler. Water flow, temperature, and the buildup of biofilm on the sampler surfaces can affect sampling rates.

Deploying passive samplers containing media spiked with performance reference compounds (PRCs) at the sample sites is one means to address these environmental variables. PRCs are chemicals added to the sampler during fabrication. By measuring the amount of PRCs lost during deployment in the field, adjustments to the sampling rates of targeted chemicals can be made to reflect the site-specific sampling rates (Alvarez 2010).

Choosing analytes with known site-specific sampling rates would allow for the determination of time-weighted average concentrations. This would provide the measurement unit conversion necessary for concentration comparisons between samples taken from the three sampling methods and therefore provide additional information on ambient concentrations. For the passive sampling devices, time-weighted averages of analyte concentration are sufficient for determining biological exposure rates.

For test protocols that measure estrogenicity and androgenicity, the high level of color in Florida waters caused interference in detections. An increased understanding of site-specific sampling rates for estrogenic and androgenic compounds and further refinement of the laboratory methods used for the determination of estrogenicity and androgenicity are recommended for future studies.

Future studies of EC in Florida's waterbodies should focus on waterbodies directly affected by known EC sources (e.g., river segments continually impacted by wastewater overflows). This will allow DEP to tailor the analyte list and sampling methods for known compounds. Additional studies should be used to determine the waterbodies for EC sampling (e.g., those known to have

water quality impairments because of biological metrics for which no known pollutant is identified).

To study bioaccumulative effects and address concerns related to public health, a fish and sediment study could provide information on the persistence of EC. Such a study could pair grab samples with biological community (e.g., fish, invertebrates) monitoring to provide information on the current state of the ecosystem and insight into what concentrations affect a targeted community. Finally, periodic statewide sample surveys for indicators of EC should be conducted so that the extent of waters impacted by these compounds can be tracked.

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Appendices

Appendix A. All Compounds Included in This Study

Pesticide Compounds Analyzed by SGS AXYS Lab

- 2,4'-DDD
- 2,4'-DDE
- 2,4'-DDT
- 4,4'-DDD
- 4,4'-DDE
- 4,4'-DDT
- Alachlor
- Aldrin
- alpha-Endosulphan
- Ametryn
- Atrazine
- Azinphos-Methyl
- beta-Endosulphan
- Butralin
- Butylate
- Captan
- Chlordane, alpha (cis)
- Chlordane, gamma (trans)
- Chlordane, oxy-
- Chlorothalonil
- Chlorpyrifos
- Chlorpyrifos-Methyl
- Chlorpyrifos-Oxon
- Cyanazine
- Cypermethrin
- Dacthal
- Desethylatrazine
- Diazinon
- Diazinon-Oxon
- Dieldrin
- Dimethenamid
- Dimethoate
- Disulfoton
- Disulfoton Sulfone
- Endosulphan Sulphate
- Endrin
- Endrin Ketone
- Ethalfluralin
- Ethion
- Fenitrothion
- Flufenacet
- Flutriafol
- Fonofos
- HCH, alpha
- HCH, beta
- HCH, delta
- HCH, gamma
- Heptachlor
- Heptachlor Epoxide
- Hexachlorobenzene
- Hexazinone
- Linuron
- Malathion
- Methoprene
- Methoxychlor
- Metolachlor
- Metribuzin
- Mirex
- Nonachlor, cis-
- Nonachlor, trans-
- Octachlorostyrene
- Parathion-Ethyl
- Parathion-Methyl
- Pendimethalin
- Permethrin
- Perthane
- Phorate
- Phosmet
- Pirimiphos-Methyl
- Quintozene
- Simazine
- Tebuconazol
- Tecnazene
- Terbufos
- Triallate
- Trifluralin

PPCP Compounds Analyzed by SGS AXYS Lab

- 1,7-Dimethylxanthine
- 10-hydroxy-amitriptyline
- 2-Hydroxy-ibuprofen
- Acetaminophen
- Albuterol
- Alprazolam
- Amitriptyline
- Amlodipine
- Amphetamine
- Amsacrine
- Atenolol
- Atorvastatin
- Azathioprine
- Azithromycin
- Benzoylcegonine
- Benztropine
- Betamethasone
- Bisphenol A
- Busulfan
- Caffeine
- Carbadox
- Carbamazepine
- Cefotaxime
- Cimetidine
- Ciprofloxacin
- Citalopram
- Clarithromycin
- Clinafloxacin
- Clonidine
- Clotrimazole
- Cloxacillin
- Cocaine
- Codeine
- Colchicine
- Cotinine
- Cyclophosphamide
- Daunorubicin
- DEET
- Dehydronifedipine
- Desmethyl-diltiazem
- Diatrizoic acid
- Diazepam
- Digoxigenin
- Digoxin
- Diltiazem
- Diphenhydramine
- Doxorubicin
- Drospirenone
- Enalapril
- Enrofloxacin
- Erythromycin-H₂O
- Etoposide
- Flumequine
- Fluocinonide
- Fluoxetine
- Fluticasone propionate
- Furosemide
- Gemfibrozil
- Glipizide
- Glyburide
- Hydrochloro-thiazide
- Hydrocodone
- Hydrocortisone
- Ibuprofen
- Iopamidol
- Lincomycin
- Lomefloxacin
- Medroxy-progesterone Acetate
- Melphalan
- Meprobamate
- Metformin
- Methyl-prednisolone
- Metoprolol
- Metronidazole
- Miconazole
- Moxifloxacin
- Naproxen
- Norfloxacin
- Norfluoxetine
- Norgestimate
- Norverapamil
- Ofloxacin
- Ormetoprim
- Oxacillin
- Oxazepam
- Oxolinic Acid
- Oxycodone
- Paroxetine
- Penicillin G
- Penicillin V
- Prednisolone
- Prednisone
- Promethazine
- Propoxyphene
- Propranolol
- Ranitidine
- Rosuvastatin
- Roxithromycin
- Sarafloxacin
- Sertraline
- Simvastatin
- Sulfachloro-pyridazine
- Sulfadiazine
- Sulfadimethoxine
- Sulfamerazine
- Sulfamethazine
- Sulfamethizole
- Sulfamethoxazole
- Sulfanilamide
- Sulfathiazole
- Tamoxifen
- Teniposide
- Theophylline
- Thiabendazole
- Trenbolone
- Trenbolone acetate
- Triamterene
- Triclocarban
- Triclosan
- Trimethoprim
- Tylosin
- Valsartan
- Venlafaxine
- Verapamil
- Virginiamycin M1
- Warfarin
- Zidovudine

Hormone Compounds Analyzed by SGS AXYS Lab

- 17 alpha-Dihydroequilin
- 17 alpha-Estradiol
- 17 alpha-Ethinyl-Estradiol
- 17 beta-Estradiol
- Allyl Trenbolone
- Androstenedione
- Androsterone
- Desogestrel
- Equilenin
- Equilin
- Estriol
- Estrone
- Mestranol
- Norethindrone
- Norgestrel
- Progesterone
- Testosterone

PFC Compounds Analyzed by SGS AXYS Lab

- Pentafluorobenzoic acid (PFBA)
- Perfluorobutanesulfonic acid (PFBS)
- Perfluorodecanoic acid (PFDA)
- Perfluorododecanoic acid (PFDoA)
- Perfluoroheptanoic acid (PFHpA)
- Perfluorohexanoic acid (PFHxA)
- Perfluorohexanesulfonic acid (PFHxS)
- Perfluorononanoic acid (PFNA)
- Perfluorooctanoic acid (PFOA)
- Perfluorooctanesulfonic acid (PFOS)
- Perfluorooctanesulfonamide (PFOSA)
- Perfluoro-n-pentanoic acid (PFPeA)
- Perfluoroundecanoic acid (PFUnA)

PBDE Compounds Analyzed by SGS AXYS Lab

- 2,2',3,3',4,4',5,5',6,6'-DeBDE
- 2,2',3,4,4',5',6-HpBDE
- 2,2',4,4',5,5'-HxBDE
- 2,2',4,4',5,6'-HxBDE
- 2,2',4,4',5-PeBDE
- 2,2',4,4',6-PeBDE
- 2,2',4,4'-TeBDE
- 2,4,4'-TriBDE

Alkylphenol Compounds Analyzed by SGS AXYS Lab

- 4-n-Octylphenol
- 4-Nonylphenol diethoxylates
- 4-Nonylphenol monoethoxylates
- 4-Nonylphenols

Pesticide Compounds Analyzed by DEP Lab

- 2,4-D
- 3-Hydroxycarbofuran
- Acetochlor
- Alachlor
- Aldicarb
- Aldicarb Sulfone
- Aldicarb Sulfoxide
- Aldrin
- Alpha-BHC
- Alpha-Chlordane
- Ametryn
- Atrazine
- Atrazine Desethyl
- Azinphos Methyl
- Bentazon
- Beta-BHC
- Bromacil
- Butylate
- Carbaryl
- Carbofuran
- Carbophenothion
- Chlordane
- Chlorothalonil
- Chlorpyrifos Ethyl
- Chlorpyrifos Methyl
- Cyanazine
- Cypermethrin
- DDD-p,p'
- DDE-p,p'
- DDT-p,p'
- Delta-BHC
- Demeton
- Diazinon
- Dicofol
- Dieldrin
- Disulfoton
- Diuron
- Endosulfan I
- Endosulfan II
- Endosulfan Sulfate
- Endrin
- Endrin Aldehyde
- Endrin Ketone
- EPTC
- Ethion
- Ethoprop
- Fenamiphos
- Fenuron
- Fipronil
- Fipronil Sulfide
- Fipronil Sulfone
- Fluridone
- Fonofos
- Gamma-BHC
- Gamma-Chlordane
- Glyphosate*
- Heptachlor
- Heptachlor Epoxide
- Hexazinone
- Imidacloprid
- Linuron
- Malathion
- MCPP
- Metalaxyl
- Methiocarb
- Methomyl
- Methoxychlor
- Metolachlor
- Metribuzin
- Mevinphos
- Mirex
- Molinate
- Norflurazon
- Oxamyl
- Parathion Ethyl
- Parathion Methyl
- Pendimethalin
- Permethrin
- Phorate
- Prometon
- Prometryn
- Propoxur
- Simazine
- Terbufos
- Terbutylazine
- Toxaphene
- Triclopyr
- Trifluralin

PPCP Compounds Analyzed by DEP Lab

- Acetaminophen
- Carbamazepine
- Primidone
- Sucralose

Appendix B. Detected Analytes

SGS AXYS Lab – Pesticides

V = Data qualified because of lab blank detection. (Blank value > 10 % of sample value.)

G = Data qualified because of field blank detection. (Blank value > 10 % of sample value.)

* Light yellow shading and asterisk are used to highlight compounds detected at all sites (N = 4).

** Dark blue shading and double asterisk are used to highlight compounds not detected at any sites, for each sample type.

§ = Presence uncertain because of high analyte concentration in blanks. (Blank value > 90 % of sample value for all sites with detections.)

Compound	SPMD # Sites with Detects	POCIS # Sites with Detects	Grab # Sites with Detects
2,4'-DDD	4*	0**	0**
4,4'-DDD	4*	0**	0**
2,4'-DDE	3	0**	0**
4,4'-DDE	4*	0**	1
4,4'-DDT	4*	0**	0**
Alachlor	1	1	1 (100% VG)
Aldrin	4 (75% V)*	1	2
Ametryn	0**	1	0**
Atrazine	2	4*	4*
Chlordane, alpha (cis)	4*	2	0**
Chlordane, gamma (trans)	4 (75% G)*	4 (100% G)	3 (100% V)
Chlordane, oxy-	4 (100% VG)*	0**	2 (100% V)
Chlorpyrifos	4	0**	1
Desethylatrazine	0**	4*	4*
Diazinon	1	1	0**
Dieldrin	4*	4*	4*
Dimethenamid	1	3	3
Endosulphan, alpha	4 (100% VG)§	4 (100% VG)§*	4 (100% VG)*
Endosulphan, beta	4 (100% VG)*	3 (100% VG)§	4 (100% VG)§*
Endosulphan Sulphate	4*	4*	3
Endrin	4 (75% V, 100% G)*	0**	2 (100% V)§

Compound	SPMD # Sites with Detects	POCIS # Sites with Detects	Grab # Sites with Detects
Endrin Ketone	2	0**	1 (100% G)§
Ethalfuralin	3	0**	0**
Flufenacet	1	0**	0**
Flutriafol	0**	1	1 (100% G)
HCH, alpha	4*	2	1
HCH, beta	4*	3	3
HCH, delta	2	1	0**
HCH, gamma	4 (100% G)*	3	1
Heptachlor	4 (100% G)*	4 (100% G)*	0**
Heptachlor Epoxide	4 (50% V)*	4 (100% G)*	3 (100% VG)
Hexachlorobenzene	4 (100% G)*	4 (100% VG)*	4 (100% VG)*
Hexazinone	0**	1	2
Metolachlor	4 (100% G)*	4	4 (25% V)*
Mirex	4 (100% VG)*	1	3
Nonachlor, cis-	4 (25% G)*	0**	1 (100% G)
Nonachlor, trans-	4	4	2
Pendimethalin	4	0**	0**
Quintozene	3 (100% G)§	3 (100% G)§	0**
Simazine	0**	4*	4*
Tebuconazol	3 (100% G)	4*	4*
Trifluralin	4*	1	0**

SGS AXYS Lab – Pharmaceuticals and PPCPs

V = Data qualified because of lab blank detection. (Blank value > 10 % of sample value.)

G = Data qualified because of field blank detection. (Blank value > 10 % of sample value.)

* Light yellow shading and asterisk are used to highlight compounds detected at all sites (N = 4).

** Dark blue shading and double asterisk are used to highlight compounds not detected at any sites, for each sample type.

§ = Presence uncertain because of high analyte concentration in blanks. (Blank value > 90 % of sample value for all sites with detections.)

Analytical lists: APOS/APOSX/APOSY = Acid extraction, positive electrospray ionization; ANEG = Acid extraction, negative electrospray ionization; BPOS = Base extraction, positive electrospray ionization

Compound	List	POCIS # Sites with Detects	Grab # Sites with Detects
Alprazolam	APOSX	4*	0**
Amitriptyline	APOSX	2	4*
Amphetamine	BPOS	4 (100% VG) [§] *	4 (100% VG)*
Atenolol	BPOS	2	3
Azithromycin	APOS	1	0**
Caffeine	APOS	0**	2
Carbamazepine	APOS	4*	3
Clarithromycin	APOS	1	0**
Cocaine	APOSX	3	2
Colchicine	APOSY	0**	2
Cotinine	BPOS	0**	2
DEET	APOSX	4*	4 (50% VG)*
Dehydronifedipine	APOS	1	1
Desmethyldiltiazem	APOSX	2	0**
Diatrizoic acid	APOSY	0**	2
Diazepam	APOSX	1	0**
Diltiazem	APOS	2	1
Diphenhydramine	APOS	1	1
Erythromycin-H2O	APOS	4*	0**
Furosemide	ANEG	0**	1

Compound	List	POCIS # Sites with Detects	Grab # Sites with Detects
Gemfibrozil	ANEG	3	0**
Hydrochlorothiazide	ANEG	1	0**
Hydrocodone	BPOS	3	0**
Iopamidol	APOSY	0**	3
Meprobamate	APOSX	0**	2
Metformin	BPOS	0**	3 (100% G)
Metoprolol	APOSX	3	0**
Naproxen	ANEG	3	3
Oxolinic Acid	APOS	1	1
Oxycodone	BPOS	3	0**
Propoxyphene	APOSX	1	0**
Sertraline	APOSX	1	1
Sulfadimethoxine	APOS	1	0**
Sulfamethazine	APOS	1	0**
Sulfamethoxazole	APOS	4*	4*
Triamterene	BPOS	3	1
Trimethoprim	APOS	3	0**
Valsartan	APOSX	2	1
Venlafaxine	APOSY	3	2

SGS AXYS Lab – Hormones

V = Data qualified because of lab blank detection. (Blank value > 10 % of sample value.)

G = Data qualified because of field blank detection. (Blank value > 10 % of sample value.)

* Light yellow shading and asterisk are used to highlight compounds detected at all sites (N = 4).

** Dark blue shading and double asterisk are used to highlight compounds not detected at any sites, for each sample type.

Compound	POCIS # Sites with Detects	Grab # Sites with Detects
Allyl Trenbolone	2	0**
Androstenedione	3	0**
Androsterone	2	2 (100% G)
Mestranol	2	4 (100% VG)*
Testosterone	1	0**

SGS AXYS Lab – PFCs

* Light yellow shading and asterisk are used to highlight compounds detected at all sites (N = 4).

** Dark blue shading and double asterisk are used to highlight compounds not detected at any sites, for each sample type.

Compound	Acronym	POCIS # Sites with Detects	Grab # Sites with Detects
Perfluorobutanoate	PFBA	0**	2
Perfluorobutanesulfonic acid	PFBS	1	1
Perfluorodecanoic acid	PFDA	2	0**
Perfluoroheptanoic acid	PFHpA	4*	2
Perfluorohexanoic acid	PFHxA	1	2
Perfluorohexanesulfonic acid	PFHxS	3	0**
Perfluorononanoic acid	PFNA	2	0**
Perfluorooctanoic acid	PFOA	4*	2
Perfluorooctanesulfonic acid	PFOS	4*	1
Perfluoropentanoate	PFPeA	0**	2

SGS AXYS Lab – PBDEs

V = Data qualified because of lab blank detection. (Blank value > 10 % of sample value.)

G = Data qualified because of field blank detection. (Blank value > 10 % of sample value.)

* Light yellow shading and asterisk are used to highlight compounds detected at all sites (N = 4) for each sample type.

§ = Presence uncertain because of high analyte concentration in blanks. (Blank value > 90 % of sample value for all sites with detections.)

Compound	SPMD # Sites with Detects	Grab # Sites with Detects
2,2',3,3',4,4',5,5',6,6'-DeBDE	4 (100% VG)§	4 (100% G)*
2,2',3,4,4',5',6-HpBDE	4 (100% G)*	3 (100% G)
2,2',4,4',5,5'-HxBDE	4 (100% G)*	2
2,2',4,4',5,6'-HxBDE	4 (100% G)*	3 (100% G)
2,2',4,4',5-PeBDE	4 (100% G)*	4 (100% VG)*
2,2',4,4',6-PeBDE	4 (100% G)*	4 (100% VG)*
2,2',4,4'-TeBDE	4 (100% G)*	4 (100% VG)*
2,4,4'-TriBDE	4 (100% G)*	2 (100% G)§

SGS AXYS Lab – Alkylphenols

V = Data qualified because of lab blank detection. (Blank value > 10 % of sample value.)

G = Data qualified because of field blank detection. (Blank value > 10 % of sample value.)

* Light yellow shading and asterisk are used to highlight compounds detected at all sites (N = 4).

** Dark blue shading and double asterisk are used to highlight compounds not detected at any sites, for each sample type.

Compound	SPMD # Sites with Detects	Grab # Sites with Detects
4-Nonylphenol diethoxylates	4 (100% G)*	0**
4-Nonylphenols	4 (100% G, 25% V)*	4 (100% VG)*

DEP Lab – Pesticides and Pharmaceuticals and PPCPs

N/A = Analysis not performed for corresponding sample type.

* Light yellow shading and asterisk are used to highlight compounds detected at all sites (N = 4).

** Dark blue shading and double asterisk are used to highlight compounds not detected at any sites, for each sample type.

Compound	SPMD # Sites with Detects	POCIS # Sites with Detects	Grab # Sites with Detects
2,4-D	0**	2	3
Acetaminophen	0**	0**	2
Acetochlor	0**	3	3
Ametryn	0**	0**	1
Atrazine	0**	4*	4*
Atrazine Desethyl	0**	0**	4*
Bentazon	0**	1	4*
Bromacil	0**	4*	4*
Carbamazepine	0**	4*	4*
Chlordane	3	N/A**	0**
Chlordane (alpha)	3	N/A**	0**
Chlordane (gamma)	2	N/A**	0**
Chlorpyrifos Ethyl	4	0**	1
DDD-p,p'	2	N/A**	0**
DDE-p,p'	3	N/A**	0**
Dieldrin	2	N/A**	0**

Compound	SPMD # Sites with Detects	POCIS # Sites with Detects	Grab # Sites with Detects
Fipronil	0**	1	3
Fipronil Sulfide	0**	0**	1
Fipronil Sulfone	0**	0**	4*
Fluridone	0**	3	3
Diuron	0**	4*	4*
Hexazinone	0**	0**	4*
Imidacloprid	0**	4*	4*
Metalaxyl	0**	4*	4*
Metolachlor	2	4*	4*
Norflurazon	0**	1	2
Pendimethalin	2	0**	0**
Prometon	0**	2	2
Simazine	0**	4*	4*
Sucralose	1	4*	4*
Toxaphene	2	N/A**	0**
Trifluralin	2	N/A**	0**