

**South Carolina Water Resources Center  
Annual Technical Report  
FY 2015**

# Introduction

The South Carolina Water Resources Center uses its operating funds to carry out its mission as a liaison between the US Geological Survey, the university community and the water resources constituencies of those institutions. This is accomplished by serving as a water resources information outlet through our web site, by serving as a research facilitator through our annual grants competition and by operating as a catalyst for research and educational projects and programs across South Carolina. The Water Center also serves as a conduit for information necessary in the resource management decision-making arena as well as the water policy arena of the state.

A reorganization across Clemson University's campus has created an opportunity to grow the Water Resources Center to meet the needs of both the university and the Center's clientele across the state. The first step in this reorganization included administrative placement of the Water Resources Center within the Public Service and Agriculture unit of Clemson. Following steps include bringing both the Clemson EPA Center for Watershed Excellence and the Clemson Institute of Environmental Toxicology (CIET) under the supervision of the Water Resources Center while physically locating all three units in the CIET building. This administrative and physical placement will streamline services these three groups provide to their clientele as well as promote a collegial atmosphere for productive cutting edge research.

Working with the Clemson University Water-Energy Consortium World Class Research Strengths at Clemson University

At Clemson University, the College of Engineering and the College of Agriculture possess considerable expertise and experience in providing scientific and engineering solutions to this grand challenge of global food and water security. Besides relevant expertise in water and food science and technologies, Clemson faculty members also embody broader expertise in resource management/policy/planning, social science, sensors/monitoring, and resource informatics.

With the successful establishment of a Water-Energy Consortium (WEC) at Clemson (<http://www.clemson.edu/ces/departments/wec/>), an effort is now underway to create/implement a counterpart Water-Food Consortium. Within these consortia, there are over 30 Clemson faculty members working within the domain of the water-energy-food nexus within the following areas: Agricultural Water Use, Quality, and Treatment; Plant Science and Genetics; Soil Science and Hydrogeology; Water and Soil Informatics; Biofuels (including Algal-Based Biofuels); Decision Support Systems and Systems Modeling; Resource Management, Policy, and Economics; Sustainability and Life Cycle Assessment; and Public Perception and Acceptance. The land-grant university status of Clemson has created unique clusters of agriculture and water research expertise and activities. Moreover, Clemson has an extensive national and international network of academic, government, and industry partners. The proposed strategic research agenda to meet this grand challenge will be performed through the framework of a reorganized water institute, potentially named the Clemson University Institute for Water Resources.

The SCWRC has continued work on a project funded through the South Carolina Sea Grant Consortium in developing the first state of the knowledge report for storm-water pond management in coastal South Carolina. The SCWRC has also been working with one of the states largest water utilities to be part of a master planning effort which will guide the growth of the Greenville, SC water system through the 21st century.

The SCWRC continues to work with key individuals from the South Carolina Department of Natural Resources, the South Carolina Department of Health and Environmental Control and South Carolina Sea Grant Consortium in order to advise these state agencies that have critical roles in managing the water resources of the state. The SCWRC has continued work as a committee member on the Savannah River Basin

Advisory Committee for SCDHEC. In addition, the SCWRC is assuming a leadership role with Clemson University's Intelligent River program, a program funded through the National Science Foundation and Clemson University that is designing real time monitoring for South Carolina's rivers. The SCWRC also sits on the South Carolina Sea Grant Consortium's Program Advisory Board and is actively involved on a project with Sea Grant to investigate alternatives to beach renourishment for communities threatened by sea level rise.

In its relationship with the South Carolina Department of Natural Resources and the South Carolina Department of Health and Environmental Control, the SCWRC has collaborated on developing a framework for a new water plan for the state of South Carolina. Water supply plans vary in their content depending on need and governmental mandate. There are some basic elements that appear in all regional plans, including an assessment of existing supply, water demand forecasting based on population and economic sector projections with assumptions and scenarios, demand side control measures, and plan implementation, monitoring and evaluation. For the South Carolina water planning effort, SCDHEC and SCDNR is providing a clear and concise mandate with specific objectives for regional and statewide water plans. The SCWRC is facilitating a stakeholder driven process to derive water sustainability objectives, develop and execute a consistent and uniform approach for engaging stakeholders in developing regional water plans, utilize a systemic approach to integrate emerging water monitoring technologies for a cost effective program, carefully evaluate economic development opportunities by region, and foster a public private partnership for process management and funding.

In South Carolina, surface water models have not yet been developed for most of the state. Through the SCWRC stakeholder process, SCDNR and SCDHEC, have begun implementing the first "whole system," basin-wide surface water availability assessment with consultant, CDM Smith. Each surface water model will be an individual basin assessment, though accounting for inter-basin transfers, withdrawals and discharges. This data collection, model development, calibration and stakeholder engagement process should be finished near the end of 2016. Stakeholder engagement is critical to this process, as the models will be available for regulators, utilities and others, with training to be made available at the conclusion of this effort. Clemson University has demonstrated statewide leadership in addressing water resource issues through focused research and education programs, statewide Extension Service programs, development of an EPA-Designated Center for Watershed Excellence, and hosting the statewide biennial South Carolina Water Resources Conference to address water issues impacting multiple stakeholders.

Finally, The SCWRC has taken over a lead role in the planning of the South Carolina Water Conference. The previous South Carolina Water Conferences have been held in 2008, 2010 and 2012. The most recent conference was held in October of 2014 with the SCWRC being an active co-sponsor while leading and running the Water Policy and Planning track of papers and presentations. The Water Center is a sponsor, evaluates presentations, moderates all water policy tracks, and encourages graduate student presentations and research. Following the 2014 conference the director of the SCWRC was named chairman of the 2016 conference. Work has continued to put together a premier conference schedule and has raised more sponsorship dollars than in any other previous conference year. In 2014, the conference published the first issue of the South Carolina Water Resources Journal based upon papers from the past conference. A 2015 issue was published based upon an open call for articles and a 2016 issue will again be produced based upon the 2016 Water Conference. The SCWRC has been an active participant in getting the journal started and the director is one of five editors for the journal.

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The SC Water Resources Center has recently been placed under the Vice-President Public Service and Agriculture (PSA). Clemson University PSA is part of a national network of 50 major land-grant universities - one in each state - that work in concert with the USDA National Institute of Food and Agriculture. Clemson PSA has state and federal mandates to conduct research, extension and regulatory programs that support economic growth in South Carolina and improved, sustained management solutions of one of our state's most important natural resources – water.

In its land grant mission to best serve the public and improve and sustain a high quality of life, water research and the dissemination of critical water knowledge is a priority for Clemson University, and not just during times of drought or extreme storms. To more effectively reach clientele with relevant and proactive research-based information, a strategy has been developed that includes the unification of several existing entities under one institute in a renovated space, need-based hires, growth opportunities for existing personnel, and refilling of vacated positions.

Water resources are critical at the local, State, National, and global level. Proper management of our water resources is not only necessary for protecting public health, maintaining ecosystem services, and protecting our food supply, but is also a critical economic development issue. Few other grand challenges require the need for an interdisciplinary approach as much as water resource management. The SC Water Resources Center will lead the effort to unite existing successful water-based programming and research efforts with faculty support and need-based hires. By way of this strategy, and with feedback from stakeholders engaged across the state, expertise will be sought in Agricultural Water Use, Quality, and Treatment; Plant Science and Genetics; Soil Science and Hydrogeology; Water and Soil Informatics; Biofuels (including Algal-Based Biofuels); Decision Support Systems and Systems Modeling; Resource Management, Policy, and Economics; Sustainability and Life Cycle Assessment; and Public Perception and Acceptance.

The SCWRC has become an active member of Clemson University's Water-Energy Consortium (WEC). The Water-Energy Consortium is a multidisciplinary group of CU faculty members, designated as WEC Fellows, who have assembled their knowledge and expertise to address an important global challenge: the Water-Energy Nexus. The nexus between water and energy encompasses energy aspects of water systems (energy footprint of water production), and water aspects of energy systems (water footprint of energy production). Besides the direct connection between water and energy, the WEC takes a broader perspective on sustainability, involving reduction of greenhouse gas (GHG) emissions and the environmental impact of both water and energy systems. While low unit costs are important, they are only part of the decision-landscape of sustainable water and energy systems. Added considerations are technology resilience within the context of climate change, and technology adaptation within the context of different climatic (temperate, arid, and tropical) regions.

The SCWRC and the WEC recently was invited by the National Science Foundation to submit a full proposal under the Partnerships for International Research and Education (PIRE) program. SCWRC and the Clemson WEC intend to partner with scientists at the University of Southern California as well as in South Korea, Singapore and Saudi Arabia to develop new membrane technologies for desalination processes as well as understand the policy processes either promoting or inhibiting use of desalination in multiple countries. Proposals are also being prepared for the NSF Innovations at the Nexus of Food, Energy and Water Systems (INFEWS) program as well as the USDA Agriculture and Food Research Initiative Water for Agriculture Challenge Area.

The SCWRC has partnered with the Greenville Water System (GWS), one of the three largest water providers in South Carolina, to assist two consulting firms with producing a new master plan for the operation of GWS

## Research Program Introduction

for the next fifty years. Phase one of this planning process has been completed with phase two planned to begin by mid 2016. This plan will impact water use for the entire western half of South Carolina. The SCWRC is also midway through a contract with the SCDNR and the SCDHEC to implement a stakeholder engagement process for the new water assessment and water plan for the state of South Carolina.

This past year the Water Center funded two research studies: 1) “Effect of Climate and Land Use Change on Water Availability for the Savannah River Basin” with Ashok Mishra (Clemson University) as principal investigator; and 2) “A Preliminary Investigation into the Ecology, Hydrodynamics, and Limnological Parameters of Oxbow Lakes in the Middle and Lower Savannah River Basin” with John Haines (Clemson University) as principal investigator and Oscar Flight (Phinizy Center for Water Sciences) as co-principal investigator.

This coming year the Water Center intends to oversee the funding of two research studies: 1) “The Influence of Poultry Rearing Facilities on Nutrient Concentrations, Fecal Indicator Bacteria, and Stream Fish in the Upper Savannah River Basin” with Gregory Lewis (Furman University) as principal investigator and Dennis Haney, Min-Ken Liao (Furman University) and Peter van den Hurk (Clemson University) as co-principal investigators; and 2) “Monitoring of Organic Pollutants in the Savannah, Edisto and Ogeechee Rivers Using Passive Samplers in Combination with a Real-time Water Quality Data Collection Network” with Peter van den Hurk (Clemson University) as principal investigator and Oscar Flight (Phinizy Center for Water Sciences) as co-principal investigator.

# Human and Ecological Health Impacts Associated with Water Reuse: Engineered Systems for Removing Priority Emerging Contaminants

## Basic Information

<b>Title:</b>	Human and Ecological Health Impacts Associated with Water Reuse: Engineered Systems for Removing Priority Emerging Contaminants
<b>Project Number:</b>	2015SC101G
<b>USGS Grant Number:</b>	
<b>Start Date:</b>	9/1/2015
<b>End Date:</b>	8/31/2016
<b>Funding Source:</b>	104G
<b>Congressional District:</b>	SC-006
<b>Research Category:</b>	Engineering
<b>Focus Category:</b>	Treatment, Toxic Substances, Surface Water
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Susan D Richardson, Dionysios Dionysiou, Daniel Schlenk

## Publications

There are no publications.

# Human and Ecological Health Impacts Associated with Water Reuse: Engineered Systems for Removing Priority Emerging Contaminants

## Initial Progress Report

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**Daniel Schlenk, Department of Environmental Sciences, University of California, Riverside**

Consistent with our proposal, the goals of our project are to:

- (1) Investigate the potential human and ecological health impacts from exposure to priority emerging contaminants (ECs) from water reuse systems using engineered systems, and
- (2) Optimize advanced oxidation technologies (AOTs) to minimize human and ecological toxicity.

This project focuses on 21 priority emerging contaminants listed in Table 1.

**The main hypothesis** is that priority emerging contaminants from wastewater effluent mixtures will be removed/transformed to a different extent in the advanced oxidation technologies vs. an advanced wastewater treatment plant (WWTP) and that the resulting toxicities will be different, due to the contribution of different contaminant levels and species.

**Table 1. Priority Emerging Contaminants (see Appendix for structures)**

Analyte
Bis(2-ethylhexylphthalate)
Bisphenol A
Bifenthrin
Butylbenzyl phthalate
Chlorpyrifos
Diclofenac
17 $\alpha$ -Ethinyl estradiol (EE2)
17 $\alpha$ -Estradiol
17 $\beta$ -Estradiol (E2)
Erythromycin
Estrone (E1)
Galaxolide (HCCB)
Ibuprofen
<i>N</i> -Nitrosodimethyl-amine (NDMA)
<i>p</i> -Nonylphenol
Perfluorooctanoic acid (PFOA)
Perfluorooctane sulfonate (PFOS)
Permethrin
Polybrominated diphenyl ether (PBDE)-47
Polybrominated diphenyl ether (PBDE)-99
Triclosan

## I. Progress To-Date

### Overview

**Team coordination.** Subawards were completed and signed with University of Cincinnati and the University of California-Riverside at the end of January 2016. We held a kick-off conference call in early February 2016 with all collaborators (including Keith Loftin from USGS and Gianluca Li Puma from Loughborough University) to discuss plans and initial work, and since that time, we have been in frequent contact by email. We also touched base with our Scientific Advisory Board to let them know we received the grant and that we will plan a meeting with them as the project progresses. We will continue to have regular conference calls and closely coordinate our activities as outlined in our proposal. In addition, we are currently scheduling Keith Loftin (USGS) to visit the USC lab in the August-September timeframe to enable analytical method development guidance and insights into the results of initial experiments, as outlined in his letter of support/collaboration. We will also coordinate a small subset of samples for interlaboratory comparison between USC and the USGS labs.

### Preliminary data: University of South Carolina (USC)

The USC team has begun both analytical methods work, as well as initial fate studies of emerging contaminants (ECs).

**1.1. Analytical methods.** Analytical methods for analyzing the parent EC molecules and their fate with advanced oxidation processes have been nearly completed. Methods for those analytes that can be measured using liquid chromatography (LC)-mass spectrometry (MS)-MS have been developed using a Thermo Orbitrap Velos Pro mass spectrometer, which will enable high resolution-MS data (up to 120,000 resolution) for the unknown transformation products (TPs)/disinfection by-products (DBPs), as well as analyzing for the loss of the parent molecule. In addition, we recently obtained a new ultraperformance liquid chromatograph (UPLC)-triple quadrupole mass spectrometer (Waters Zevo), which will also be used for MS-MS analyses. Methods for those analytes that can be measured using gas chromatography (GC)-MS have been developed using a LECO Pegasus HRT high resolution time-of-flight mass spectrometer (with Agilent 7890 gas chromatograph), which allows up to 50,000 resolution. High resolution-MS (with both GC and LC) are important for generating empirical formulas for the molecular ions and fragment ions for the TPs and DBPs to enable their identification (as described in our preliminary experiments below). Further methods information is provided in the Appendix. Upon completion, our analytical methods will also be shared with our partners at the University of Cincinnati for quantification of target contaminants during treatment.

**1.2. Preliminary fate experiments.** In preparation for upcoming experiments with the Orange County Ground Water Replenishment System (GWRS) waters, initial controlled laboratory experiments are being conducted using chlorine, as described in our proposal. Because source waters, including those from Orange County, can also contain bromide, which leads to formation of brominated species upon chlorination, bromide was also added in separate experiments to analyze for bromine-containing DBPs.

**1.3. Reaction conditions.** Chlorination reactions were conducted at pH 7 (using phosphate buffer) by adding chlorine (0.813 M) to 25 mL of Milli-Q water containing appropriate amounts of analyte (Table 2) to achieve a 20:1 ratio (100 mM chlorine and 5 mM analyte) of chlorine to analyte. These experiments were also repeated using the addition of sodium bromide (10 mM) to investigate the potential formation of brominated DBPs. Each sample was split into two 60 mL amber vials (one with headspace (40 mL), one without (60 mL)) and put on a mechanical shaker for 30 minutes. The samples were allowed to react at room temperature for 72 hours. All reactions were performed in duplicate. Two sets of controls were also carried out. The first set involved adding chlorine (and bromide for the brominated control) to buffered Milli-Q water and carrying out reactions as for the real samples. The second set involved adding analyte only to buffered water, without the addition of chlorine and/or bromide.

**Table 2. Emerging contaminants reacted with chlorine**

Compound	Analyte Amount (mg) → 5 mM solution
Bisphenol A	114
Triclosan	145
Estrone (E1)	135
17 $\beta$ -Estradiol (E2)	136
17 $\alpha$ -Ethinyl estradiol (EE2)	148

**1.4. Extractions.** Samples for LC-MS-MS analysis were extracted using solid phase extraction (SPE) with Oasis HLB cartridges (6 cc). The SPE cartridges were conditioned with 3 mL of a 1:1 methanol:acetone mixture, followed by 1 mL of Milli-Q water with buffer. The cartridges were loaded with sample under vacuum. Samples were then dried using nitrogen for 30 min, eluted using 3 mL of 1:1 methanol:acetone, and concentrated to 2 mL with nitrogen. The extracts were diluted further by mixing 700  $\mu$ L Milli-Q water to 300  $\mu$ L of extract in an LC vial. The samples were then analyzed using a Thermo Orbitrap mass spectrometer.

Samples for GC-MS analysis (10 mL reacted headspace-free) were extracted using liquid-liquid extraction (3x) with dichloromethane (3.3 mL). A separatory funnel was used to remove water; sodium sulfate was added to the extract remove any remaining water. Extracts were analyzed using the LECO high resolution time-of-flight mass spectrometer.

**1.5. LC-MS-MS and GC-MS Conditions.** A Thermo Orbitrap Velos Pro mass spectrometer with HESI-II electrospray (ESI) source was used for the LC-MS-MS analyses, along with a Dionex Ultimate 3000 liquid chromatograph and an Agilent Zorbax-SB-C18 column (5  $\mu$ M, 0.5 x 150 mm). A gradient LC program was used with water/acetonitrile (30% water:acetonitrile to 95% acetonitrile in 35 min), 12  $\mu$ L/min flow rate, and 1  $\mu$ L sample injected. Samples were analyzed in negative ESI mode at 60,000 resolution, using a probe temperature of 100  $^{\circ}$ C and spray voltage of -2500 V. Tandem mass spectrometry experiments (collisionally induced dissociation, CID) were conducted in the linear ion trap portion of the instrument. Collision energies were optimized (10-50 eV) to obtain sufficient fragment (product) ions to enable identification of emerging contaminant DBPs.

A LECO Pegasus HRT high resolution time-of-flight mass spectrometer with Agilent 7890 gas chromatograph was used for GC-MS analyses. A Restek Rxi-5ms GC column was used (30 m x 25 mm ID) under constant flow (1 mL/min) and splitless injection of 1.0  $\mu$ L of sample. The injection port temperature was controlled at 230  $^{\circ}$ C and transfer line at 280  $^{\circ}$ C. The GC program consisted of a 35  $^{\circ}$ C hold for 4 minutes, a ramp of 9  $^{\circ}$ C/min to 280  $^{\circ}$ C, and a final hold at 15 minutes. Electron ionization mode was used with a source temperature of 200  $^{\circ}$ C and m/z range of 30-510.

Tentative structural assignments for unknown DBPs were made using the following: (1) NIST library database searching; (2) assessment of halogen isotopic patterns to determine the type and number of halogens present; (3) accurate mass and empirical formula assignments for the molecular ion and fragment ions; (4) ChemSpider searching for chemical structures matching molecular formula assignments; and (5) careful interpretation of fragment ions. Authentic standards will be purchased or synthesized to confirm as many DBPs as possible, through a match of their mass spectra and retention times.

**2.1. LC-MS-MS data.** Several disinfection by-products (DBPs) were tentatively identified using LC-high resolution-MS-MS using the Orbitrap mass spectrometer. For bisphenol A (BPA), they included monochloro-, dichloro-, trichloro-, and tetrachloro-BPA (Figure 1). To determine which isomers these were, separate reactions were also carried out using deuterated ( $d_4$ )-BPA, which was deuterated at the carbons *ortho* to the hydroxyl groups. Use of this deuterated standard allowed precise isomers to be identified, highlighting the site of chlorine substitution (Figure 1). Several brominated DBPs of BPA were also observed in the chlorination reactions that included added bromide, including bromo-trichloro-BPA, dibromo-dichloro-BPA, tetrabromo-BPA, tribromo-BPA, dibromo-BPA, and monobromo-BPA. The mass spectrum of the bromo-trichloro-BPA product is shown in Figure 2.

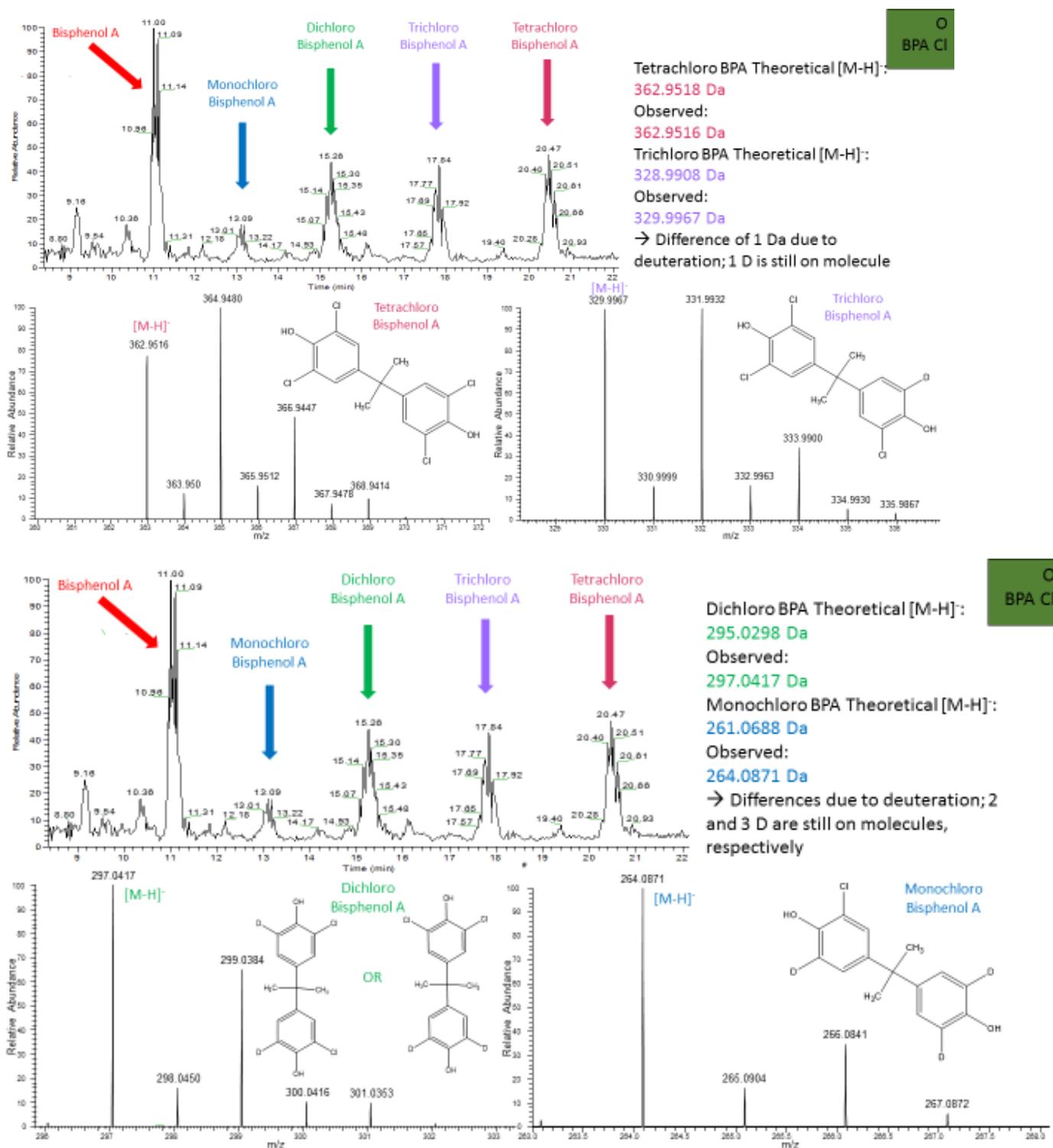


Figure 1. LC-MS-MS chromatogram and high resolution ESI mass spectra of DBPs formed by the reaction of bisphenol A and deuterated ( $d_4$ ) bisphenol A with chlorine.

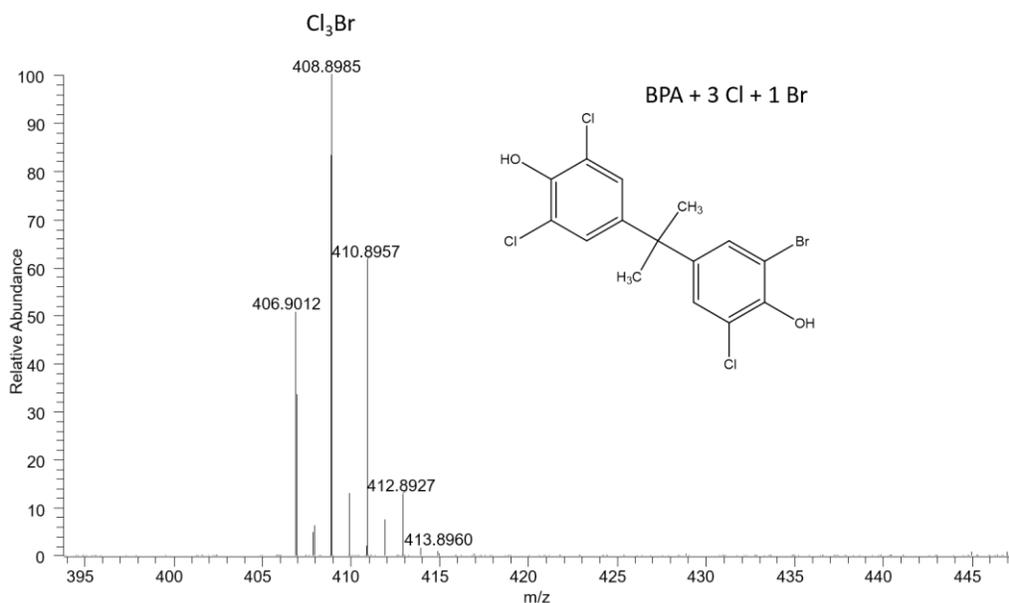
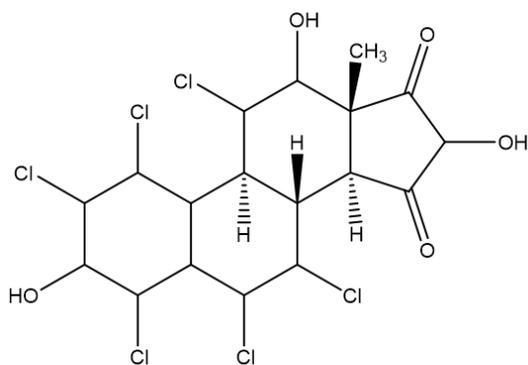
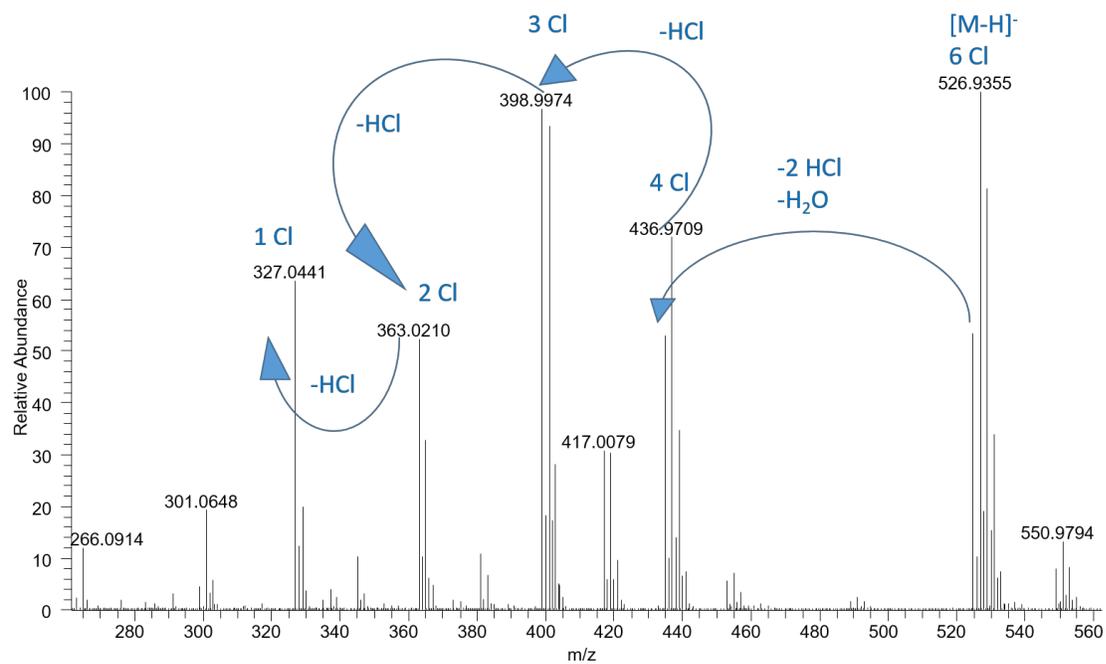
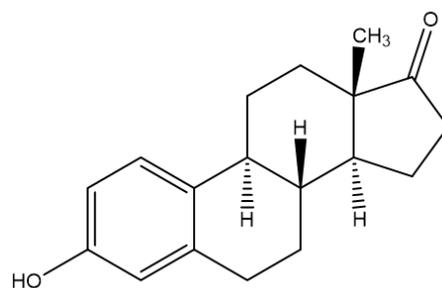


Figure 2. Negative ion ESI mass spectrum of a bisphenol A (BPA) DBP formed by reaction with chlorine and added bromide. The halogen pattern for 3 chlorines and 1 bromine is evident (bromo-trichloro-BPA). The empirical formula observed matches the theoretical formula (theoretical  $[M-H]^-$  is 406.9013). Analyses carried out on the LC-Orbitrap mass spectrometer.

Chlorinated DBPs were also observed for estrone (E1) by LC-ESI-MS-MS. An example is shown in Figure 3, in which the DBP formed gained six chlorines in its structure. The halogen patterns are also evident, as well as the neutral losses. A possible structure is proposed. Similarly, DBPs were evident in the LC-MS-MS data for triclosan. It should be noted that triclosan contains three chlorines in its original chemical structure, and accordingly, it shows a 3-chlorine isotopic pattern for its molecular ion in the negative ion ESI mass spectrum (Figure 4). An example of one of the DBPs tentatively identified and its MS-MS spectrum is shown in Figure 5. The 4-chlorine isotopic pattern is evident in this product.



Possible structure for E1  
+ 6 Cl and oxidized  
 $C_{18}H_{20}O_5Cl_6$



Estrone (E1)  
 $C_{18}H_{22}O_2$

Figure 3. Mass spectrum of chlorinated estrone (E1) DBP. A possible structure is proposed.

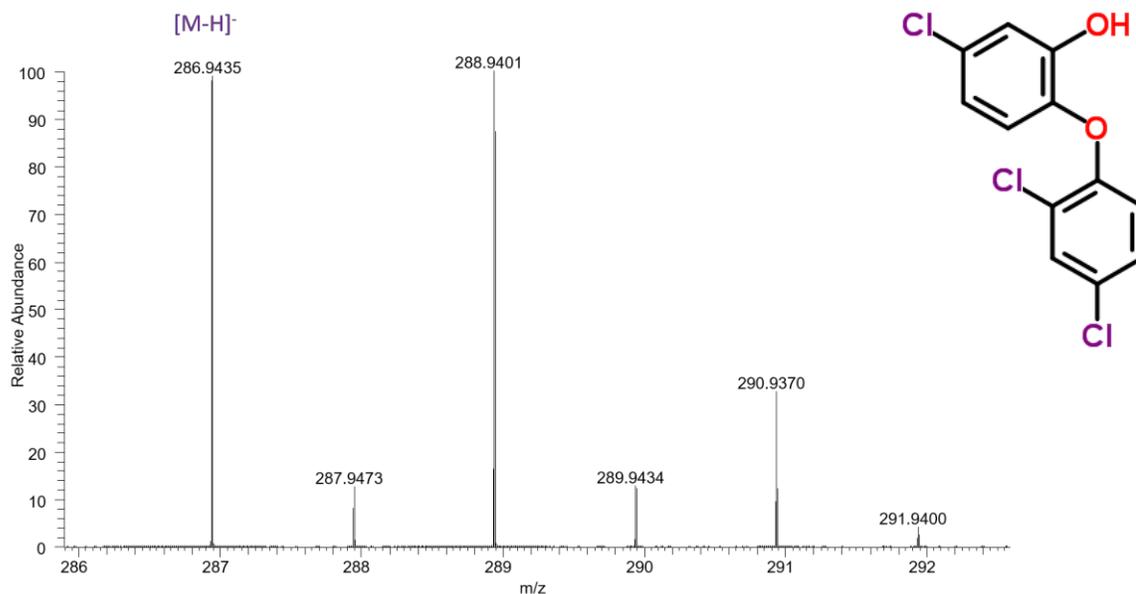


Figure 4. Mass spectrum of triclosan. While DBPs of triclosan were observed following reaction with chlorine for 72 hours, the parent molecule of triclosan was still present. Because it was analyzed in negative ESI, [M-H]<sup>-</sup> is observed rather than [M+H]<sup>+</sup>.

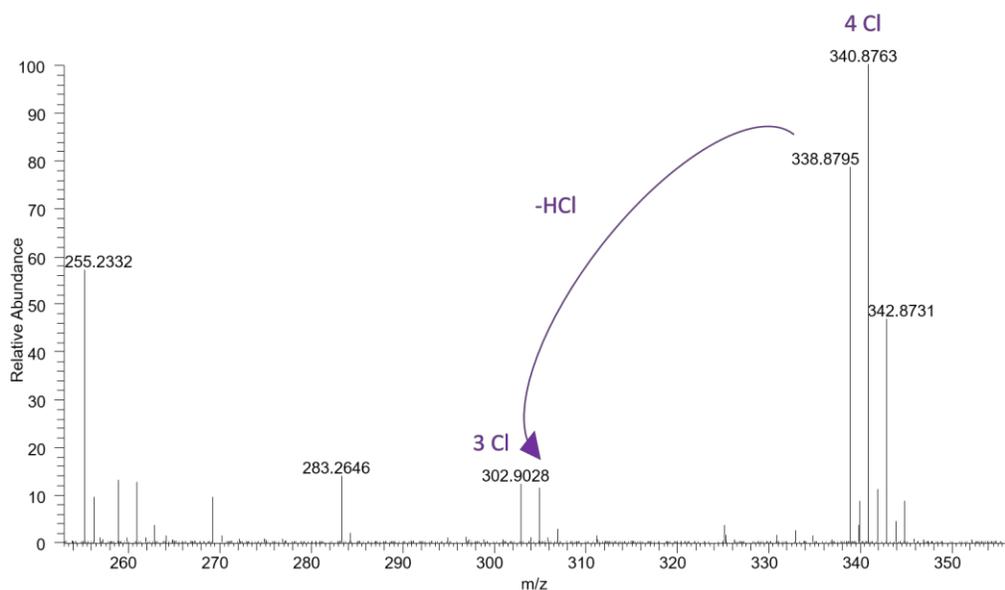


Figure 5. Mass spectrum of DBP formed in chlorination reactions of triclosan. Triclosan has three chlorines in its chemical structure; this spectrum's halogen patterns and neutral losses show that it gained an additional chlorine during the reaction. The molecule's strong aromaticity aids chlorine addition.

**3.1. GC-MS data.** Several DBPs were also tentatively identified using GC with high resolution-MS with the LECO high resolution time-of-flight mass spectrometer. For estrone reactions, these include bromodichloromethane, dibromochloromethane, 2-chloro-4-methyl-(R\*,S\*)-(n)-3-pentanol, 1,2-dichloro-2-methylbutane, and 1,1-dichloro-2,3-dimethylcyclopropane. For ethinyl estradiol (EE2) reactions, these include 1-chloro-2-propanone, 2-chloro-3-methyl-2-butene, 2,3-dimethyl-3-hexanol, 2-chloromethyl-1,3-dichloro-2-methylpropane. For 17 $\beta$ -estradiol (E2), these include 3-chloro-2-methyl-1-butene. Some of these are new DBPs that have not been reported in the literature previously. Work is ongoing to identify other DBPs formed in these samples.

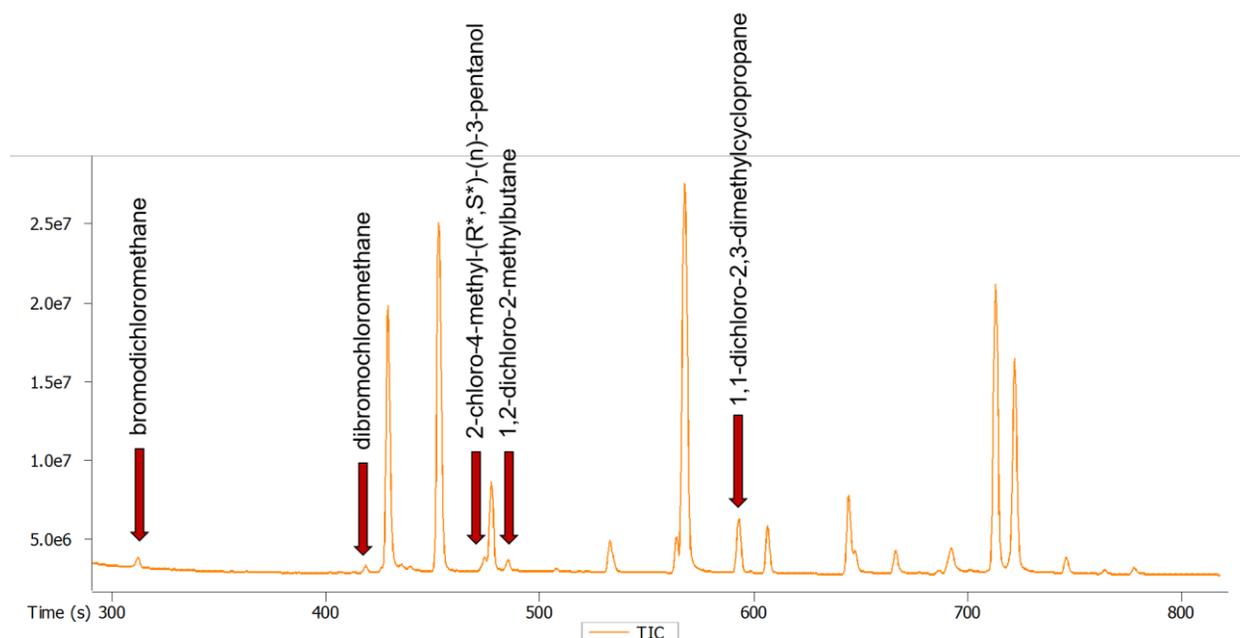


Figure 6. GC-MS chromatogram of estrone (E1) DBPs formed by reactions of chlorine with added bromide. The five selected peaks were different from the blank and had NIST library matches.

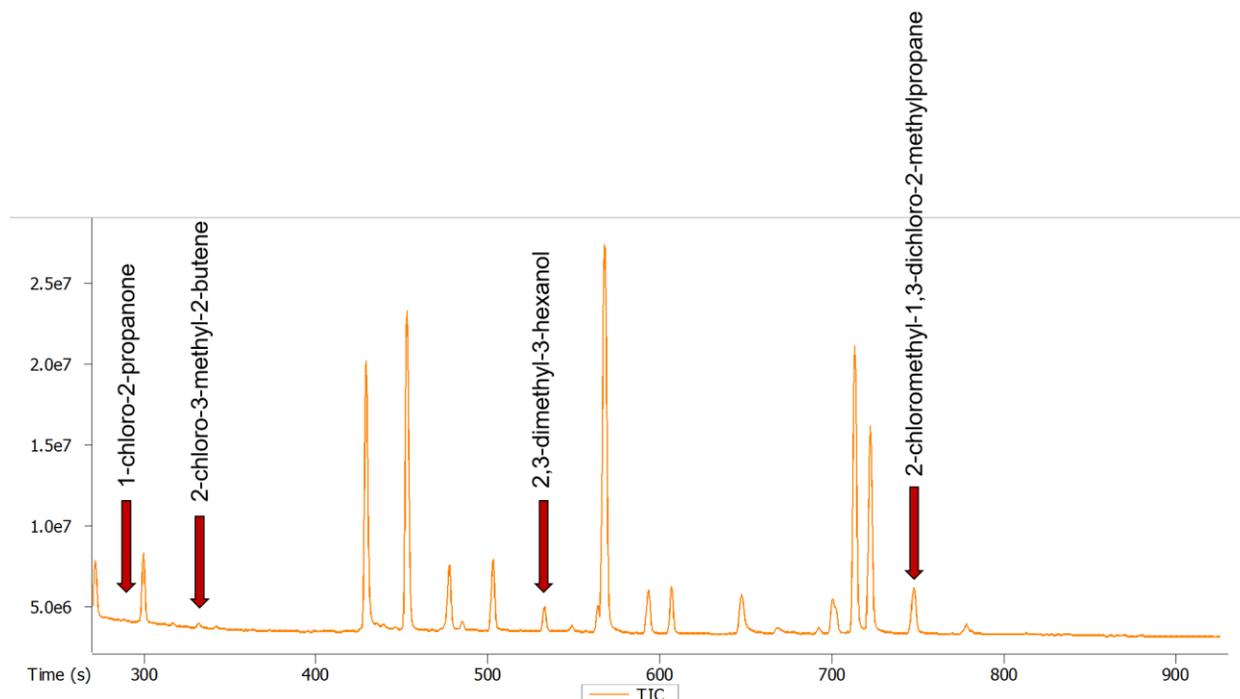


Figure 7. GC-MS chromatogram of ethinyl estradiol (EE2) DBPs formed by reactions of chlorine with added bromide. The four selected peaks were different from the blank and had NIST library matches.

### **Preliminary data: University of Cincinnati (UC)**

The UC team has begun carrying out initial degradation studies of emerging contaminants (ECs) using UV-C-H<sub>2</sub>O<sub>2</sub>. In this part, the degradation of seven ECs including diclofenac (DCF), triclosan (TCS), estrone (E1), 17 $\beta$ -estradiol (E2), 17 $\alpha$ -ethinyl estradiol (EE2), bisphenol A (BPA), and ibuprofen (IBP) by UV-C alone and UV-C/H<sub>2</sub>O<sub>2</sub> in Milli-Q water was investigated. The effect of pH and H<sub>2</sub>O<sub>2</sub> dosage on the degradation of these contaminants was also studied. Irradiation experiments were conducted in a bench-scale collimated beam system where two 15W low pressure UV (LP-UV) lamps with monochromatic emission of  $\lambda_{\text{max}} = 254$  nm were used. Moreover, the newly developed mercury-free light-emitting diode UV (LED-UV) with primary emission of 255 nm was used to replace the commonly used LP-UV to degrade these compounds, and its efficiency was compared to LP-UV. The average fluence rate of LP-UV and LED-UV were 0.1 and 0.03 mW cm<sup>-2</sup>, respectively. The concentration of all contaminants was quantified using high performance liquid chromatography (HPLC).

#### **4.1. Degradation of Diclofenac (DCF) by UV/H<sub>2</sub>O<sub>2</sub>**

##### **4.1.1. Degradation of DCF by UV alone and UV/H<sub>2</sub>O<sub>2</sub> in Milli-Q Water**

As shown in Figure 8, DCF could be degraded under UV irradiation alone, and approximately 83% of DCF was removed at a UV fluence of 320 mJ cm<sup>-2</sup>. With the addition of H<sub>2</sub>O<sub>2</sub>, the degradation

of DCF was significantly increased due to the formation of hydroxyl radicals ( $\text{HO}^\bullet$ ), as presented in Eqn (1). The degradation of DCF by UV alone and UV/ $\text{H}_2\text{O}_2$  fit pseudo first-order kinetics. The observed UV fluences, based pseudo first-order rate constants ( $k_{\text{obs}}$ ), were  $(5.62 \pm 0.19) \times 10^{-3}$  and  $(2.17 \pm 0.05) \times 10^{-2} \text{ cm}^2 \text{ mJ}^{-1}$ , for UV and UV/ $\text{H}_2\text{O}_2$ , respectively. Compared to removal of DCF by LP-UV/ $\text{H}_2\text{O}_2$ , its destruction by LED-UV/ $\text{H}_2\text{O}_2$  was comparable at the same UV fluence (Figure 8), indicating the high efficiency of LED-UV for the activation of  $\text{H}_2\text{O}_2$ .

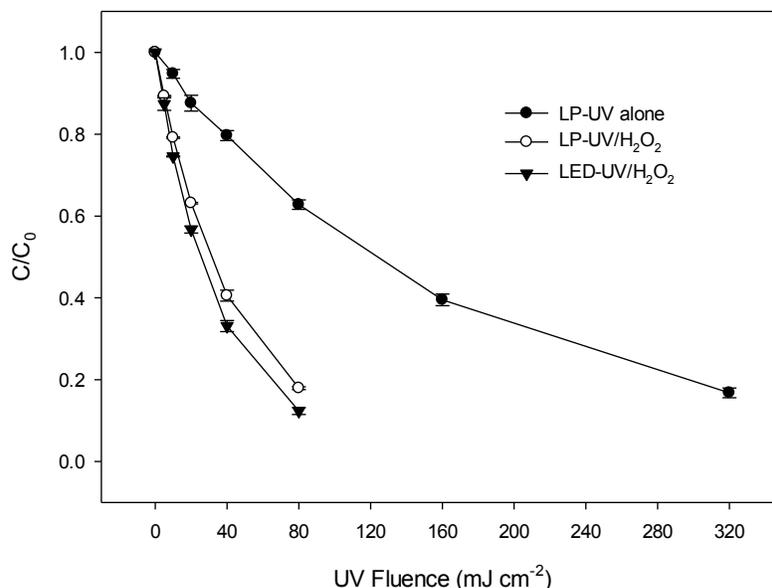
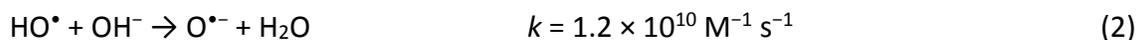


Figure 8. Degradation of DCF by UV alone and UV/ $\text{H}_2\text{O}_2$ . Experimental conditions:  $[\text{DCF}]_0 = 1 \mu\text{M}$ ,  $[\text{H}_2\text{O}_2]_0 = 1 \text{ mM}$ , no phosphate buffer.

#### 4.1.2. Effect of pH

The destruction of DCF by UV/ $\text{H}_2\text{O}_2$  included two different reaction pathways, i.e., UV direct photolysis and the oxidation of hydroxyl radical. Therefore, to investigate the effect of pH on DCF degradation by UV/ $\text{H}_2\text{O}_2$ , it is necessary to evaluate its effect by UV alone first. As presented in Figure 9(a), the photolysis of DCF under UV irradiation alone was almost the same in the studied pH conditions. The inset is the  $k_{\text{obs}}$  in the different pH values. This finding can be explained by the similar molar absorption coefficients of DCF at 254 nm in studied pH values, as shown in Figure 10. Figure 9(b) shows the influence of pH on DCF removal by UV/ $\text{H}_2\text{O}_2$ . The degradation of DCF was similar from pH 5.3 to 7.4 and decreased gradually with the increase in pH, which was attributed to the scavenging of hydroxyl radical by the increased hydroxide ion ( $\text{OH}^-$ ), as shown in Eqn. (2).



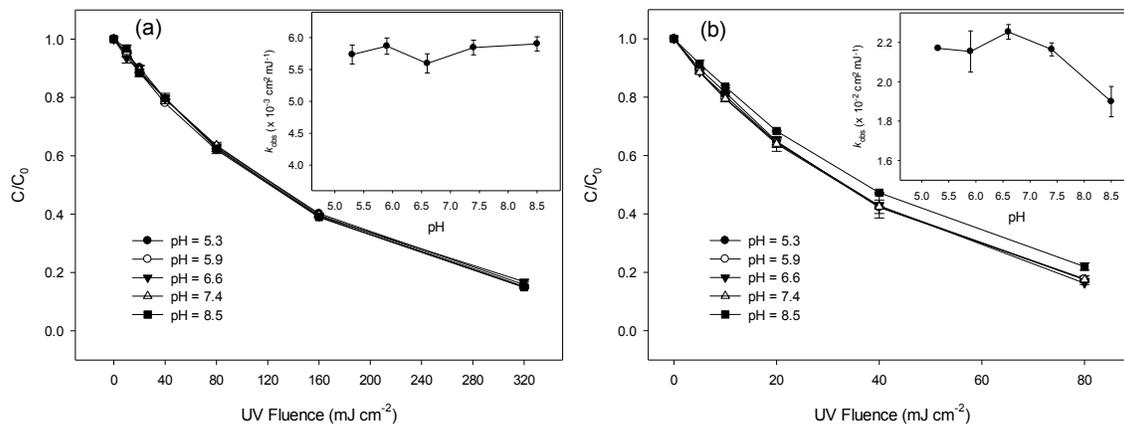


Figure 9. Effect of pH on the degradation of DCF by UV alone (a) and UV/ $\text{H}_2\text{O}_2$  (b). Experimental conditions:  $[\text{DCF}]_0 = 1 \mu\text{M}$ ,  $[\text{H}_2\text{O}_2]_0 = 1 \text{ mM}$ , 10 mM phosphate buffer.

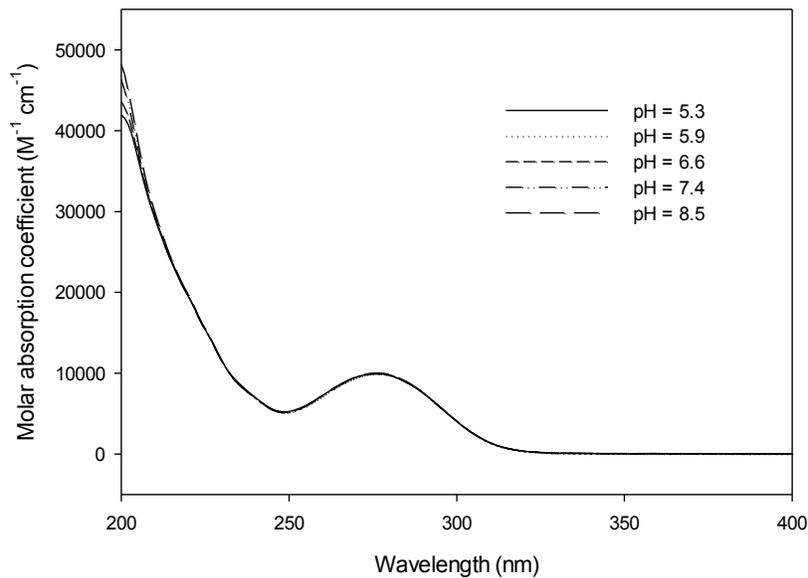


Figure 10. UV-Vis spectra of DCF in different pH values. Experimental conditions:  $[\text{DCF}]_0 = 50 \mu\text{M}$ , 10 mM phosphate buffer.

#### 4.1.3. Effect of initial $\text{H}_2\text{O}_2$ dosage

Oxidant dosage is an important parameter in evaluating the applicability of UV/ $\text{H}_2\text{O}_2$  process. Figure 11 describes the effect of initial  $\text{H}_2\text{O}_2$  dosage on the degradation of DCF. The removal of DCF increased with the increase of initial  $\text{H}_2\text{O}_2$  concentration; however, there was no linear increase of  $k_{\text{obs}}$  with the increase in  $\text{H}_2\text{O}_2$  dosage, as shown in the inset, which could probably result from the scavenging effect of the excess  $\text{H}_2\text{O}_2$ , specifically the competitive radical reactions (Eqs. (3)-(5)).

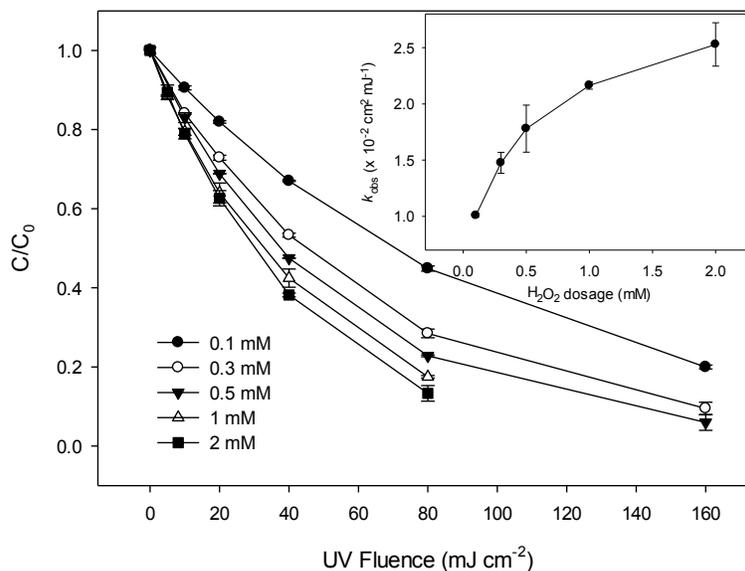
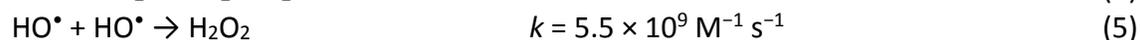
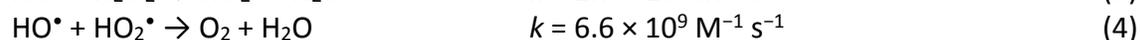
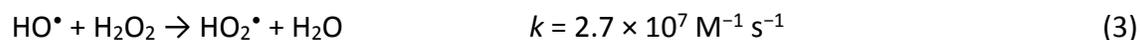


Figure 11. Effect of  $\text{H}_2\text{O}_2$  dosage on DCF degradation by UV/ $\text{H}_2\text{O}_2$ . Experimental conditions:  $[\text{DCF}]_0 = 1 \mu\text{M}$ , 10 mM phosphate buffer at pH 7.4.

## 5.1. Degradation of Triclosan (TCS) by UV/ $\text{H}_2\text{O}_2$

### 5.1.1. Degradation of TCS by UV alone and UV/ $\text{H}_2\text{O}_2$

As described in Figure 12, approximately 62% TCS was degraded at a UV fluence of  $320 \text{ mJ cm}^{-2}$  under UV irradiation alone. The destruction of TCS was enhanced significantly in the presence of  $\text{H}_2\text{O}_2$  and approximately 76% TCS was removed at a UV fluence of  $80 \text{ mJ cm}^{-2}$ . The observed UV fluence-based pseudo first-order rate constants of TCS by UV alone and UV/ $\text{H}_2\text{O}_2$  were  $(2.99 \pm 0.06) \times 10^{-3}$  and  $(1.74 \pm 0.01) \times 10^{-2} \text{ cm}^2 \text{ mJ}^{-1}$ , respectively. The degradation of TCS by LED-UV/ $\text{H}_2\text{O}_2$  and LP-UV/ $\text{H}_2\text{O}_2$  was almost the same, as shown in Figure 12, confirming again the feasibility and effectiveness of LED-UV in the activation of  $\text{H}_2\text{O}_2$ .

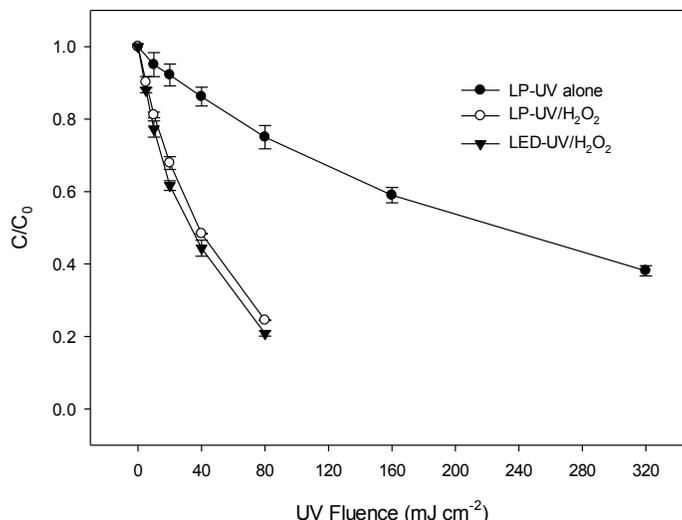


Figure 12. Degradation of TCS by UV alone and UV/H<sub>2</sub>O<sub>2</sub>. Experimental conditions: [TCS]<sub>0</sub> = 1 μM, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 1 mM, no phosphate buffer.

### 5.1.2. Effect of pH

The results on the effect of pH on TCS degradation by UV alone and UV/H<sub>2</sub>O<sub>2</sub> are presented in Figure 13. The insets are the observed UV fluence-based pseudo first-order rate constants of TCS at the current pH conditions studied. It was found that the destruction of TCS by UV alone was enhanced with an increase in pH, and  $k_{obs}$  increased from  $(2.69 \pm 0.44) \times 10^{-3}$  to  $(8.09 \pm 0.99) \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-1}$  when pH increased from 5.3 to 8.5 (Figure 13(a)). This result could probably be due to the increased molar absorption coefficients of TCS at 254 nm with the increase of pH, as shown in Figure 14. Though the concentration of OH<sup>-</sup> increased with the increase in pH, leading to the increased scavenging for hydroxyl radical (Eqn. (2)), the degradation of TCS was comparable at pH 5.3-7.4 and enhanced at pH 8.5, as described in Figure 13(b), which was probably due to the increased photolysis of TCS (Figure 13(a)).

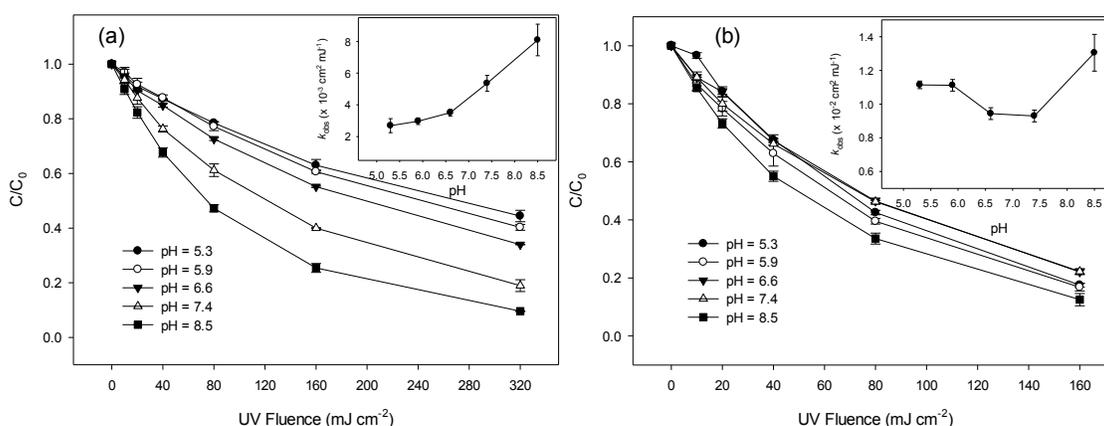


Figure 13. Effect of pH on the degradation of TCS by UV alone (a) and UV/H<sub>2</sub>O<sub>2</sub> (b). Experimental conditions: [TCS]<sub>0</sub> = 1 μM, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.3 mM, 10 mM phosphate buffer.

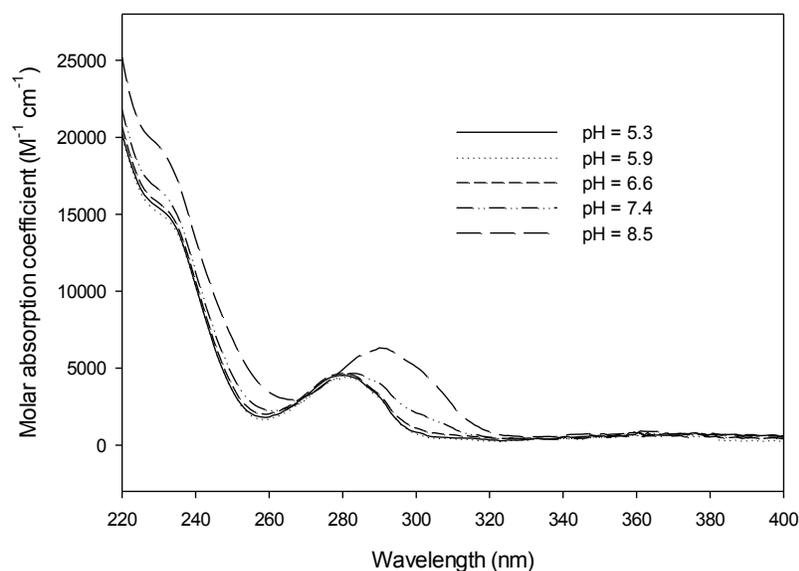


Figure 14. UV-Vis spectra of TCS in different pH values. Experimental conditions:  $[TCS]_0 = 5 \mu\text{M}$ , 10 mM phosphate buffer.

### 5.1.3. Effect of initial $\text{H}_2\text{O}_2$ dosage

The effect of initial  $\text{H}_2\text{O}_2$  dosage on TCS degradation by UV/ $\text{H}_2\text{O}_2$  is presented in Figure 15. The destruction of TCS enhanced with increased initial  $\text{H}_2\text{O}_2$  concentration. As  $\text{H}_2\text{O}_2$  dosage increased continually, the excess  $\text{H}_2\text{O}_2$  could compete with the target compound for the hydroxyl radical (Eqn. (3)), contributing to the non-linear increase of  $k_{\text{obs}}$ , as shown in the inset.

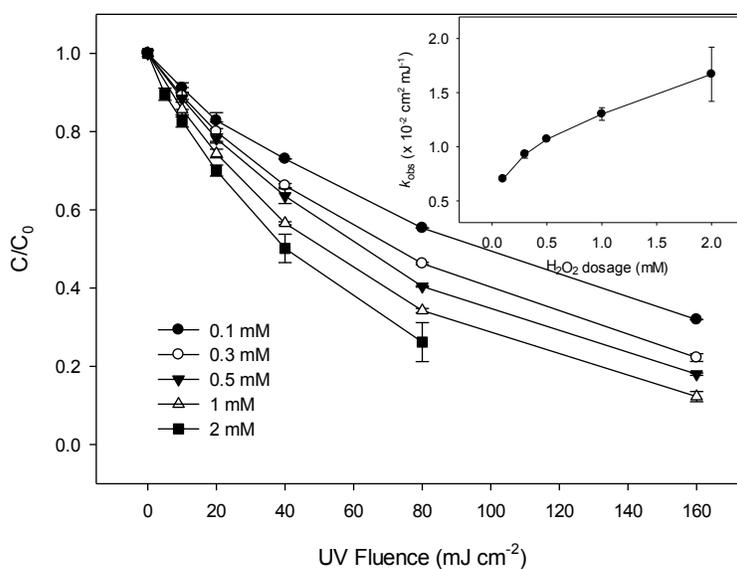


Figure 15. Effect of initial  $\text{H}_2\text{O}_2$  dosage on TCS degradation by UV/ $\text{H}_2\text{O}_2$ . Experimental conditions:  $[TCS]_0 = 1 \mu\text{M}$ , 10 mM phosphate buffer at pH 7.4.

## 6.1. Degradation of estrone (E1), 17 $\beta$ -estradiol (E2), 17 $\alpha$ -Ethinyl estradiol (EE2), bisphenol A (BPA) and ibuprofen (IBP)

### 6.1.1. Degradation of E1, E2, EE2, BPA and IBP by UV alone and UV/H<sub>2</sub>O<sub>2</sub>

The destruction of E1, E2, EE2, BPA and IBP by UV alone and UV/H<sub>2</sub>O<sub>2</sub> in Milli-Q water is shown in Figure 16. It was found that E1 and E2 could be degraded under UV irradiation (Figure 16(a) and (b)), while the photolysis of EE2, BPA and IBP was negligible within the reaction timeframe (Figure 16(c)-(e)). The observed UV fluence-based pseudo first-order rate constants of E1 and E2 by UV alone were  $(6.58 \pm 0.23) \times 10^{-4}$  and  $(4.04 \pm 0.65) \times 10^{-4}$  cm<sup>2</sup> mJ<sup>-1</sup>, respectively. With the addition of H<sub>2</sub>O<sub>2</sub>, the degradation of all these five compounds was increased significantly due to the oxidation by hydroxyl radical generated from the homolysis of H<sub>2</sub>O<sub>2</sub> under UV irradiation. The  $k_{\text{obs}}$  for E1, E2, EE2, BPA, and IBP by UV/H<sub>2</sub>O<sub>2</sub> were  $(1.24 \pm 0.17) \times 10^{-2}$ ,  $(1.12 \pm 0.03) \times 10^{-2}$ ,  $(2.04 \pm 0.14) \times 10^{-2}$ ,  $(2.10 \pm 0.26) \times 10^{-2}$ , and  $(1.90 \pm 0.28) \times 10^{-2}$  cm<sup>2</sup> mJ<sup>-1</sup>, respectively. The removals of E1, E2, and EE2 by LED-UV/H<sub>2</sub>O<sub>2</sub> were similar to those obtained by LP-UV/H<sub>2</sub>O<sub>2</sub> (Figure 16(a)-(c)), indicating again the probable practical application of LED-UV in water treatment.

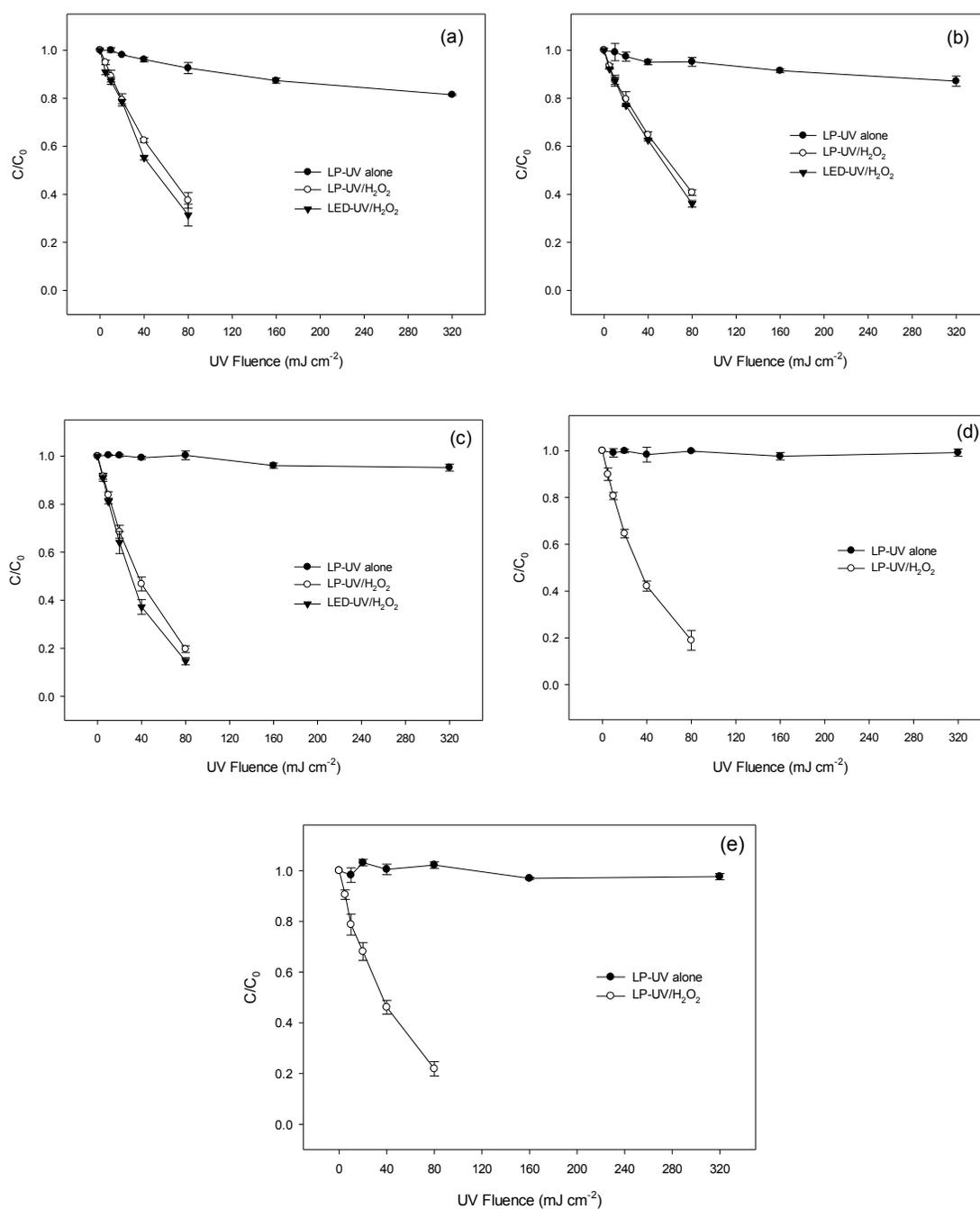


Figure 16. Degradation of E1 (a), E2 (b), EE2 (c), BPA (d), and IBP (e) by UV alone and UV/ $\text{H}_2\text{O}_2$ . Experimental conditions:  $[\text{E1}]_0 = [\text{E2}]_0 = [\text{EE2}]_0 = [\text{BPA}]_0 = [\text{IBP}]_0 = 1 \mu\text{M}$ ,  $[\text{H}_2\text{O}_2]_0 = 1 \text{mM}$ , no phosphate buffer.

### 6.1.2. Effect of pH on the degradation of E1 and E2 by UV alone

As stated above, E1 and E2 could be photolyzed under UV irradiation alone. The effect of pH on the photolysis of E1 and E2 is presented in Figure 17(a) and (b), respectively. The degradation of E1 by UV alone in the studied pH values was almost the same probably due to the same existing form ( $pK_a = 10.8$ ) and similar molar absorptivity at these different pH values. Comparing the photolysis of E2 in Milli-Q water, the destruction of E2 in phosphate buffer solutions (10 mM) at different pH was much slower, which could be ignored within the studied timescale.

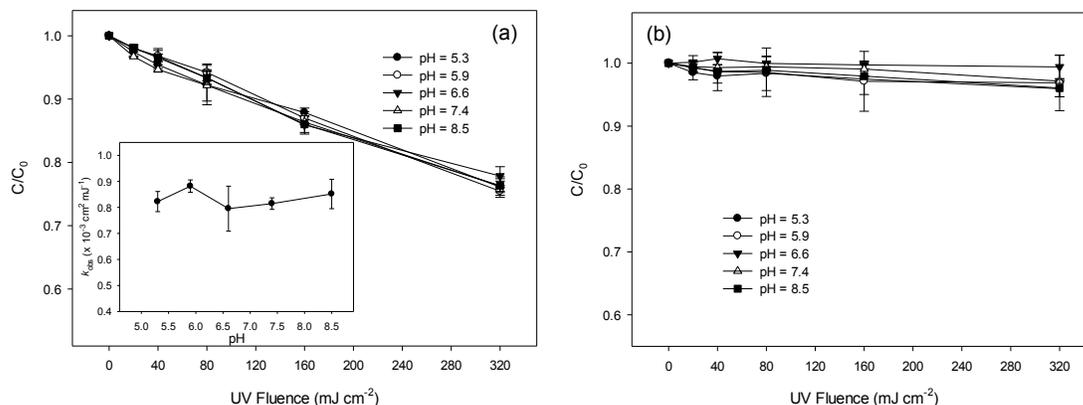


Figure 17. Effect of pH on the degradation of E1 (a) and E2 (b) by UV alone. Experimental conditions:  $[E1]_0 = [E2]_0 = 1 \mu\text{M}$ , 10 mM phosphate buffer.

### 6.1.3. Effect of pH on the degradation of E1, E2, EE2 and BPA by UV/ $\text{H}_2\text{O}_2$

Figure 18 shows the effect of pH on the destruction of E1, E2, EE2, and BPA by UV/ $\text{H}_2\text{O}_2$ . The insets are the influence of pH on their respective observed pseudo first-order rate constants. The degradation of all these four compounds was decreased with the increase in pH, probably due to the scavenging of hydroxyl radical by increased  $\text{OH}^-$  ions (Eqn. (2)).

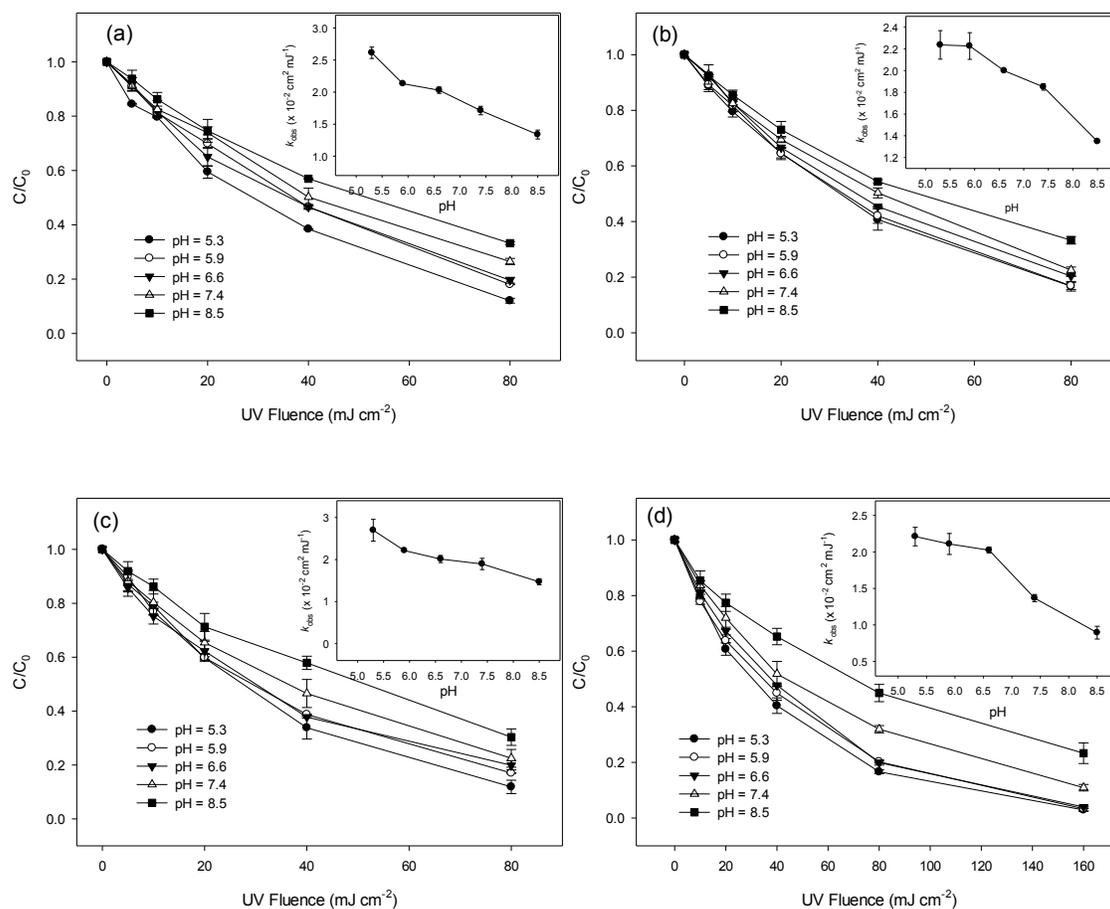


Figure 18. Effect of pH on the degradation of E1 (a), E2 (b), EE2 (c), and BPA (d) by UV/H<sub>2</sub>O<sub>2</sub>. Experimental conditions:  $[E1]_0 = [E2]_0 = [EE2]_0 = [BPA]_0 = 1 \mu\text{M}$ ,  $[H_2O_2]_0 = 1 \text{ mM}$ , 10 mM phosphate buffer.

### 7.1. Degradation of Mixed contaminants by UV/H<sub>2</sub>O<sub>2</sub>

All the results above were based on the reaction system in which there was only one contaminant. If there are several different contaminants in the UV/H<sub>2</sub>O<sub>2</sub> system, due to the reactions of these compounds with hydroxyl radical, the degradation of the target contaminant may be different from that in the system where only the target compound is present. In this part, DCF, IBP, BPA, EE2, and E1 were mixed in the same reaction solution to investigate their respective degradation by UV alone and by UV/H<sub>2</sub>O<sub>2</sub>. The results are presented in Figure 19. The destruction of IBP, BPA, and EE2 in this mixed solution under UV irradiation alone was very limited, which was in a good agreement with the discussion above. The photolysis of DCF and E1 in the current mixed system was also comparable with their respective degradation in the system in which there was only one compound. These results indicate that the degradation of these target compounds by UV alone was scarcely affected in the mixed solution where several different contaminants coexist. However, comparing the respective removal of these compounds in the system where only one contaminant is present, the degradation of all these

compounds in the UV/H<sub>2</sub>O<sub>2</sub> process was inhibited under the current reaction conditions (Figure 19), probably due to the competition for hydroxyl radical among them.

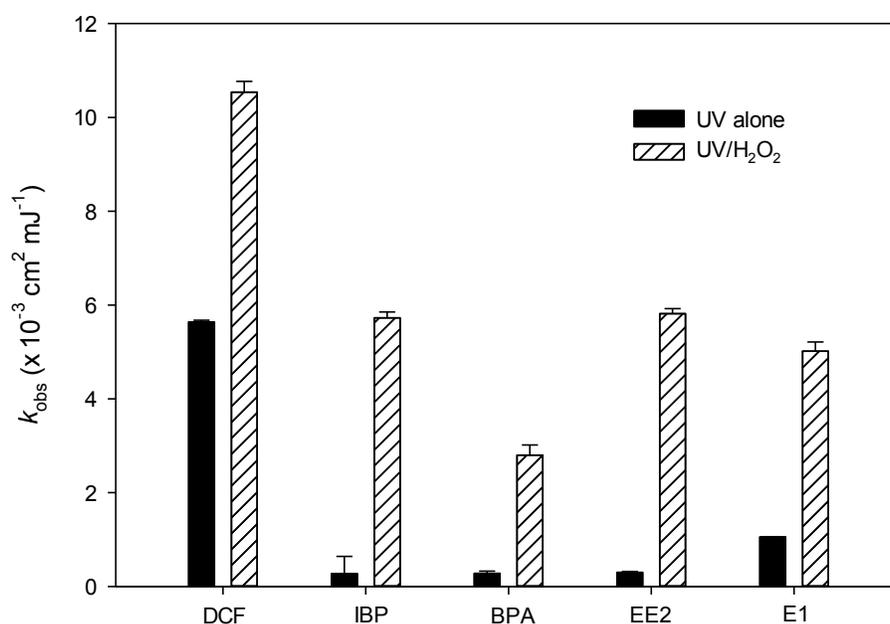


Figure 19. Degradation of mixed contaminants by UV alone and UV/H<sub>2</sub>O<sub>2</sub>. Experimental conditions: [DCF]<sub>0</sub> = [IBP]<sub>0</sub> = [BPA]<sub>0</sub> = [EE2]<sub>0</sub> = [E1]<sub>0</sub> = 1 μM, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 1 mM, no phosphate buffer.

### III. Scientific Presentations

While this project is still in its early phases, USC (Kristin Cochran) recently had the opportunity to present some of her preliminary data on this project (along with some previous EC work) at the American Society for Mass Spectrometry (ASMS) Conference held in San Antonio, TX, June 5-9, 2016. Her poster was well received, and many reprint requests were requested.

Citation: Removal and Transformation of Persisting Emerging Contaminants via Advanced Oxidation Techniques, [Kristin H Cochran](#), Jorge Casado, Danilo Russo, Danilo Spasiano, Marianna Vaccaro, Gianluca Li Puma, Roberto Andreozzi, Nuno M. Reis, Raffaele Marotta, Dionysios Dionysiou, Daniel Schlenk, and Susan D. Richardson. American Society for Mass Spectrometry Conference, San Antonio, TX. June 5-9, 2016.

### III. Next Steps

For the USC team, initial chlorination reactions were carried out with the emerging contaminants most likely to form DBPs, based on their chemical structures (e.g., presence of phenolic or other chlorine-reactive functional groups). Data analysis is ongoing for identification of other DBPs

formed in these initial reactions (as judged by the appearance of new LC-MS-MS or GC-MS peaks that were not present in the blanks). Next steps will involve conducting chlorination reactions with the remaining emerging contaminants. Analytical methods for quantifying the parent emerging contaminants will also be completed soon, also utilizing the new Waters Xevo triple quadrupole, in addition to the Thermo Orbitrap mass spectrometer.

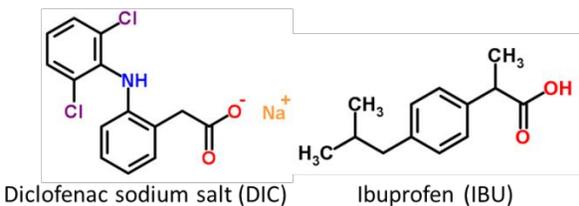
For the UC team, in the preliminary experiments, we mainly studied the degradation of each emerging contaminant using UV-C/H<sub>2</sub>O<sub>2</sub>. Next, we will mix different emerging contaminants in the same system and investigate their removal by UV-C/H<sub>2</sub>O<sub>2</sub>, UV-C/TiO<sub>2</sub>, and solar light/TiO<sub>2</sub> in Milli-Q water. The transformation products of these contaminants by UV-C/H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub> photocatalysis will also be examined and identified using LC-MS-MS and/or GC-MS.

Once these initial experiments are completed (projected to be during the next 3-6 months), we will obtain water treated with reverse osmosis from the Orange County Ground Water Replenishment System (GWRS) and conduct UV-C/H<sub>2</sub>O<sub>2</sub>, UV-C/TiO<sub>2</sub>, solar light/TiO<sub>2</sub>, and chlorination reactions, as described in the proposal. The degradation of the emerging contaminants will be investigated, as well as potential transformation products and DBPs using LC-MS-MS and GC-MS. We will also send some of these reacted samples to collaborators at UC-Riverside for cell-based toxicity measurements. Finally, as mentioned earlier, we are currently scheduling Keith Loftin from USGS to visit the USC lab for input and collaboration on our analytical methods and preliminary results. As the project progresses with the reactions of GWRS waters, we will hold a meeting with the Scientific Advisory Board (experts detailed in our proposal) to seek their feedback.

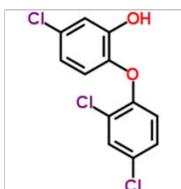
## APPENDIX

## Pharmaceuticals and Personal Care Products

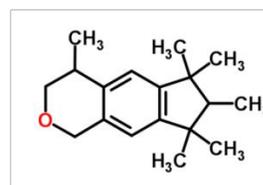
## Non-Steroidal Anti-Inflammatory Drugs (NSAIDs)



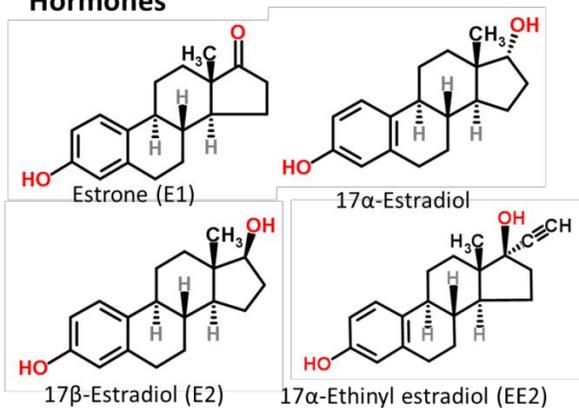
## Biocides



## Fragrances



## Hormones



## Antibiotics

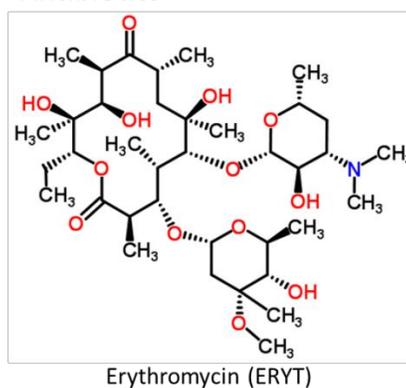
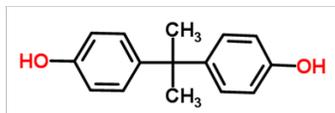


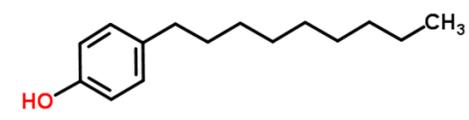
Figure 1A. Structures of Emerging Contaminants: Pharmaceuticals and Personal Care Products.

## Industrial Chemicals

### Polymer Industry

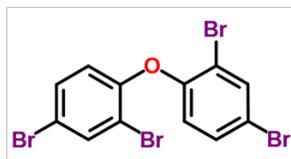


Bisphenol A (BPA)

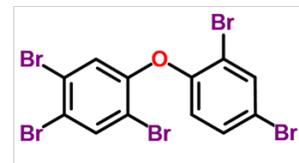


p-Nonylphenol (p-NP)

### Flame Retardants (PBDEs)

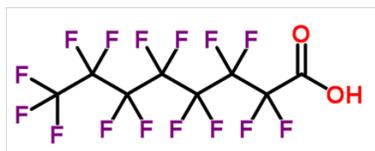


Polybrominated diphenyl ether (PBDE-47)

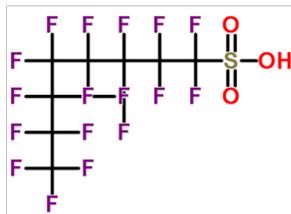


Polybrominated diphenyl ether (PBDE-99)

### Perfluorinated Compounds (PFCs)

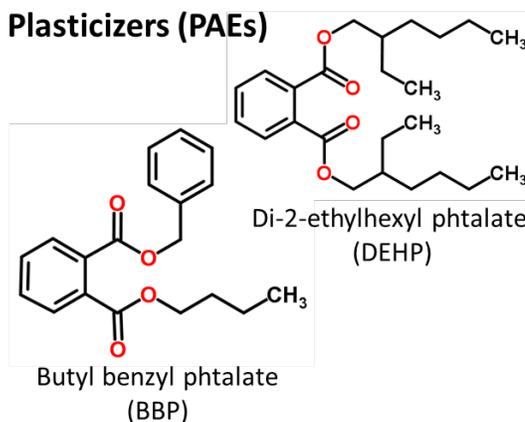


Perfluorooctanoic acid (PFOA)



Perfluorooctane sulfonate (PFOS)

### Plasticizers (PAEs)



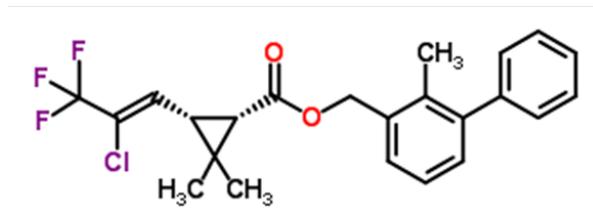
Di-2-ethylhexyl phthalate (DEHP)

Butyl benzyl phthalate (BBP)

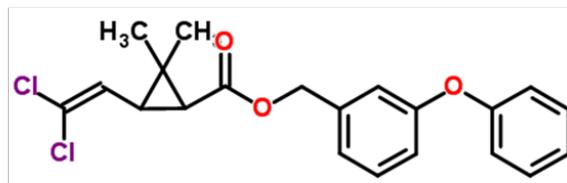
Figure 1B. Structures of Emerging Contaminants: Industrial Chemicals.

## Pesticides

### Pyrethroids

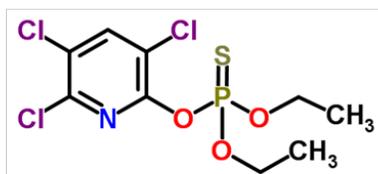


Bifenthrin (BF)



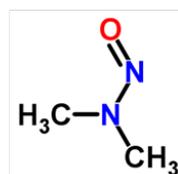
Permethrin (PER)

### Organophosphate



Chlorpyrifos (CPF)

## Disinfection By-products (DBPs)



N-Nitrosodimethylamine (NDMA)

Figure 1C. Structures of Emerging Contaminants: Pesticides and Disinfection By-Products.

## Method Optimization

Analytical standards and isotopically labeled internal standards were purchased and method optimization for quantitative measurements of the parent emerging contaminants was conducted. For analytes that are more suitable for LC-MS-MS analyses (highly polar, higher molecular weight, or non-volatile), positive ion and negative ion-ESI were evaluated, in which voltages, temperatures, and other MS and MS-MS conditions optimized, along with effect of pH and different solvents used as the LC eluent. For analytes more suitable for GC-MS analysis (volatile or semi-volatile), high resolution electron ionization-MS data were obtained and optimized.

The following includes properties of these compounds and information resulting from preliminary optimization of these methods for the parent emerging contaminants.

**Table A1. LC-MS-MS (Orbitrap) ESI+ Compounds and properties.**

Analyte	Name	CAS	MW	Formula	Log Kow	pKa	Limit	Company
ERYT	Erythromycin	114-07-8	733.93	C <sub>37</sub> H <sub>67</sub> NO <sub>13</sub>	1.9	13.1; 8.1	ng L <sup>-1</sup>	Sigma
ERYT-H2O	Anhydro Erythromycin A	23893-13-2	715.91	C <sub>37</sub> H <sub>65</sub> NO <sub>12</sub>	3.9	13.46; 8.1		TRC
DIC	Diclofenac sodium salt	15307-79-6	318.13	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> NNaO <sub>2</sub>	4.5	4.2; -2.3	ng L <sup>-1</sup>	Sigma
BBP	Butyl benzyl phtalate	85-68-7	312.36	C <sub>19</sub> H <sub>20</sub> O <sub>4</sub>	4.9		ng L <sup>-1</sup>	Sigma
CPF	Chlorpyrifos	2921-88-2	350.59	C <sub>9</sub> H <sub>11</sub> Cl <sub>3</sub> NO <sub>3</sub> PS	5	-5.3	ug L-1	Sigma
PER	Permethrin	52645-53-1	391.29	C <sub>21</sub> H <sub>20</sub> Cl <sub>2</sub> O <sub>3</sub>	7.6		ng L <sup>-1</sup>	Sigma
DEHP	Di-2-ethylhexyl phtalate	117-81-7	390.56	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	8.5		ng L <sup>-1</sup>	Sigma

**Table A2. LC-MS-MS (Orbitrap) ESI- Compounds and properties.**

Analyte	Name	CAS	MW	Formula	Log Kow	pKa	Limit	Company
<b>PFOA</b>	Perfluorooctanoic acid	335-67-1	414.07	C <sub>8</sub> HF <sub>15</sub> O <sub>2</sub>	6.4	0.5	ng L <sup>-1</sup>	Sigma
<b>BPA</b>	Bisphenol A	80-05-7	228.29	C <sub>15</sub> H <sub>16</sub> O <sub>2</sub>	3.6	10.3	ng L <sup>-1</sup>	Sigma
<b>E2</b>	17β-Estradiol	50-28-2	272.38	C <sub>18</sub> H <sub>24</sub> O <sub>2</sub>	4.1	10.3	ng L <sup>-1</sup>	Sigma
<b>α-E2</b>	17α-Estradiol	57-91-0	272.38	C <sub>18</sub> H <sub>24</sub> O <sub>2</sub>	4.1	10.3	ng L <sup>-1</sup>	Sigma
<b>PFOS</b>	Perfluorooctane sulfonate	1763-23-1	500.13	C <sub>8</sub> HF <sub>17</sub> O <sub>3</sub> S	4.5	-3.3	ng L <sup>-1</sup>	Matrix Sci
<b>EE2</b>	17α-Ethinyl estradiol	57-63-6	296.40	C <sub>20</sub> H <sub>24</sub> O <sub>2</sub>	4.1	10.2	ng L <sup>-1</sup>	Sigma
<b>E1</b>	Estrone	53-16-7	270.37	C <sub>18</sub> H <sub>22</sub> O <sub>2</sub>	3.6	10.2	ng L <sup>-1</sup>	Sigma
<b>DIC</b>	Diclofenac sodium salt	15307-79-6	318.13	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> NNaO <sub>2</sub>	4.5	4.2; -2.3	ng L <sup>-1</sup>	Sigma
<b>IBU</b>	Ibuprofen	15687-27-1	206.28	C <sub>13</sub> H <sub>18</sub> O <sub>2</sub>	3.5	4.41	ng L <sup>-1</sup>	Sigma
<b>TCS</b>	Triclosan	3380-34-5	289.54	C <sub>12</sub> H <sub>7</sub> Cl <sub>3</sub> O <sub>2</sub>	5.3	7.8	ng L <sup>-1</sup>	TRC
<b>p-NP</b>	p-Nonylphenol	104-40-5	220.35	C <sub>15</sub> H <sub>24</sub> O	6.1	10.1	ng L <sup>-1</sup>	Sigma

**Table A3. LC-MS-MS Internal Standards.**

IS	Company
<b>13C-ERYT</b>	Cambridge
<b>D4-DIC</b>	CDN
<b>D4-BBP</b>	Cambridge
<b>13C8-PFOA</b>	Cambridge
<b>D4-BPA</b>	CDN
<b>D2-E2</b>	CDN
<b>13C18-PFOS</b>	Cambridge
<b>D4-EE2</b>	CDN
<b>D2-E1</b>	CDN
<b>D3-IBU</b>	CDN
<b>D3-TCS</b>	CDN
<b>D4-pNP</b>	CDN

Table A4. LC-MS-MS ESI+ (Orbitrap) retention times, accurate masses, and MS-MS conditions

ESI +	Formula	Monoisotopic Mass (Da)	Retention time (min)	MS Full-Scan ions (Da)			MS/MS conditions			
				[M+H] <sup>+</sup>	<sup>37</sup> Cl[M+H] <sup>+</sup>	[M+Na] <sup>+</sup>	Precursor ion (Da)	Collision energy (eV)	Quantification ion (Da)	Other product ion (Da)
<b>ERYT-H2O</b>	C <sub>37</sub> H <sub>65</sub> NO <sub>12</sub>	715.4511	9.8 10.6	716.4583		738.4403	716.4583	18	558.3640	522.3402
<b>DIC</b>	C <sub>14</sub> H <sub>11</sub> Cl <sub>2</sub> NO <sub>2</sub>	295.0167	13.1	296.0240	298.0211	318.0060	296.0240	18	278.0134	250.0185
<b>BBP</b>	C <sub>19</sub> H <sub>20</sub> O <sub>4</sub>	312.1363	17.9	313.1436		335.1255	313.1436	17	149.0234	205.0860
<b>CPF</b>	C <sub>9</sub> H <sub>11</sub> Cl <sub>3</sub> NO <sub>3</sub> PS	348.9263	19.5	349.9336	351.9307	371.9156	349.9336	20	321.9023	293.8710
<b>DEHP</b>	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	390.2770	25.9	391.2845		413.2664	391.2845	18	149.0234	279.1592
<b>ERYT-<sup>13</sup>C</b>	<sup>13</sup> CC <sub>36</sub> H <sub>67</sub> NO <sub>13</sub>	734.465	8.5	735.4723		757.4542	735.4723	18	577.3779	559.3673
<b>DIC-D4</b>	C <sub>14</sub> H <sub>7</sub> D <sub>4</sub> Cl <sub>2</sub> NO <sub>2</sub>	299.0418	13.1	300.0491	302.0462	322.0310	300.0491	18	282.0385	254.0436
<b>BBP-D4</b>	C <sub>19</sub> H <sub>16</sub> D <sub>4</sub> O <sub>4</sub>	316.1614	17.9	317.1686		339.1506	317.1686	17	153.0484	209.1111

Table A5. LC-MS-MS ESI- (Orbitrap) retention times, accurate masses, and MS-MS conditions

ESI -	Formula	Monoisotopic Mass (Da)	Retention time (min)	MS Full-Scan ions (Da)		MS/MS conditions			
				[M-H]-	<sup>37</sup> Cl[M-H]-	Precursor ion (Da)	Collision energy (eV)	Quantification ion (Da)	Other product ion (Da)
PFOA	C <sub>8</sub> HF <sub>15</sub> O <sub>2</sub>	413.9737	8.9	412.9664		412.9664	11	368.9755	
BPA	C <sub>15</sub> H <sub>16</sub> O <sub>2</sub>	228.1151	10.0	227.1078		227.1078	33	212.0833	133.0648
E2 β	C <sub>18</sub> H <sub>24</sub> O <sub>2</sub>	272.1778	10.4	271.1705					
E2 α	C <sub>18</sub> H <sub>24</sub> O <sub>2</sub>	272.1778	10.8	271.1705					
PFOS branched	C <sub>8</sub> HF <sub>17</sub> O <sub>3</sub> S	499.9375	10.4	498.9302					
PFOS linear	C <sub>8</sub> HF <sub>17</sub> O <sub>3</sub> S	499.9375	10.8	498.9302					
EE2	C <sub>20</sub> H <sub>24</sub> O <sub>2</sub>	296.1778	11.1	295.1705		295.1705	40	267.1381	185.0961
E1	C <sub>18</sub> H <sub>22</sub> O <sub>2</sub>	270.1621	11.8	269.1548		269.1548	46	145.0648	
DIC	C <sub>14</sub> H <sub>11</sub> Cl <sub>2</sub> NO <sub>2</sub>	295.0167	13.0	294.0095	296.0065	294.0095	17	250.0185	
IBU	C <sub>13</sub> H <sub>18</sub> O <sub>2</sub>	206.1308	13.8	205.1235		205.1235	22	161.1326	
TCS	C <sub>12</sub> H <sub>7</sub> Cl <sub>3</sub> O <sub>2</sub>	287.9512	16.7	286.9439	288.9410				
p-NP	C <sub>15</sub> H <sub>24</sub> O	220.1828	21.1	219.1756		219.1756	38	106.0414	
PFOA- <sup>13</sup> C <sub>8</sub>	<sup>13</sup> C <sub>8</sub> HF <sub>15</sub> O <sub>2</sub>								
BPA-D4	C <sub>15</sub> H <sub>12</sub> D <sub>4</sub> O <sub>2</sub>	232.1402	10.0	231.1329		231.1329	33	216.1083	135.0774
E2 β-D2	C <sub>18</sub> H <sub>22</sub> D <sub>2</sub> O <sub>2</sub>	274.1903	10.4	273.1830					
PFOS b- <sup>13</sup> C <sub>8</sub>	<sup>13</sup> C <sub>8</sub> HF <sub>17</sub> O <sub>3</sub> S								
PFOS l- <sup>13</sup> C <sub>8</sub>	<sup>13</sup> C <sub>8</sub> HF <sub>17</sub> O <sub>3</sub> S								
EE2-D4	C <sub>20</sub> H <sub>20</sub> D <sub>4</sub> O <sub>2</sub>	300.2028	11.1	299.1956		299.1956	40	269.1506	187.1087
E1-D2	C <sub>18</sub> H <sub>20</sub> D <sub>2</sub> O <sub>2</sub>	272.1746	11.8	271.1674		271.1674	46	147.0774	
DIC-D4	C <sub>14</sub> H <sub>7</sub> D <sub>4</sub> Cl <sub>2</sub> NO <sub>2</sub>	299.0418	13.0	298.0345	300.0316	298.0345	17	254.0436	

<b>IBU-D3</b>	C <sub>13</sub> H <sub>15</sub> D <sub>3</sub> O <sub>2</sub>	209.1496	13.8	208.1423		208.1423	22	164.1514	
<b>TCS-D3</b>	C <sub>12</sub> H <sub>4</sub> D <sub>3</sub> Cl <sub>3</sub> O <sub>2</sub>	290.9700	16.7	289.9627	291.9598				
<b>p-NP-D4</b>	C <sub>15</sub> H <sub>20</sub> D <sub>4</sub> O	224.2079	21.1	223.2006		223.2006	38	110.0664	

**Table A6. GC-MS (TOF) Compounds and Properties.**

Analyte	Name	CAS	MW	Formula	Log Kow	pKa	Neutral	Limit	Company
<b>NDMA</b>	N-Nitrosodimethylamine	62-75-9	74.08	C <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O	-0.5	-3.6	-3.6<pH	ng L <sup>-1</sup>	Sigma
<b>p-NP</b>	p-Nonylphenol	104-40-5	220.35	C <sub>15</sub> H <sub>24</sub> O	6.1	10.1	pH<10.1	ng L-1	Sigma
<b>HHCB</b>	Galaxolide	1222-05-5	258.40	C <sub>18</sub> H <sub>26</sub> O	5			ng L <sup>-1</sup>	TRC
<b>CPF</b>	Chlorpyrifos	2921-88-2	350.59	C <sub>9</sub> H <sub>11</sub> Cl <sub>3</sub> NO <sub>3</sub> PS	5	-5.3	-5.3<pH	ug L-1	Sigma
<b>BPA</b>	Bisphenol A	80-05-7	228.29	C <sub>15</sub> H <sub>16</sub> O <sub>2</sub>	3.6	10.3	pH<10.3	ng L-1	Sigma
<b>BBP</b>	Butyl benzyl phthalate	85-68-7	312.36	C <sub>19</sub> H <sub>20</sub> O <sub>4</sub>	4.9			ng L <sup>-1</sup>	Sigma
<b>BF</b>	Bifenthrin	82657-04-3	422.87	C <sub>23</sub> H <sub>22</sub> ClF <sub>3</sub> O <sub>2</sub>	7.3			ng L <sup>-1</sup>	Sigma
<b>PBDE-47</b>	Polybrominated diphenyl ether	5436-43-1	485.79	C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O	6.7			pg L-1	TRC
<b>DEHP</b>	Di-2-ethylhexyl phthalate	117-81-7	390.56	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	8.5			ng L <sup>-1</sup>	Sigma
<b>PER</b>	Permethrin	52645-53-1	391.29	C <sub>21</sub> H <sub>20</sub> Cl <sub>2</sub> O <sub>3</sub>	7.6			ng L <sup>-1</sup>	Sigma
<b>PBDE-99</b>	Polybrominated diphenyl ether	60348-60-9	564.69	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	7.3			pg L-1	AccuStand

**Table A7. GC-MS Accurate Masses (Molecular Ions and Fragment Ions) and Retention Times**

<b>Analyte</b>		<b>MS Fragments</b>		<b>Ret Time (min)</b>
<b>NDMA</b>	N-Nitrosodimethylamine	74.0480	42.0218	5.63
<b>p-NP</b>	p-Nonylphenol	107.0497	220.1827	13.36
<b>HHCB</b>	Galaxolide	243.1749	213.1643	13.40
<b>CPF</b>	Chlorpyrifos	96.9513	196.9202	14.81
<b>BPA</b>	Bisphenol A	213.0916	119.0497	17.15
<b>BBP</b>	Butyl benzyl phtalate	91.0548	149.0814	19.15
<b>BF</b>	Bifenthrin	181.1017	165.0283	21.51
<b>PBDE-47</b>	Polybrominated diphenyl ether	325.8765	485.7112	22.19
<b>DEHP</b>	Di-2-ethylhexyl phtalate	149.0239	167.0344	22.46
<b>PER 1</b>	Permethrin	183.0810	163.0081	24.69
<b>PER 2</b>	Permethrin	183.0810	163.0081	24.93
<b>PBDE-99</b>	Polybrominated diphenyl ether	403.7870	563.6217	25.91

# A Preliminary Investigation into the Ecology, Hydrodynamics, and Limnological Parameters of Oxbow Lakes in the Middle and Lower Savannah River Basin

## Basic Information

<b>Title:</b>	A Preliminary Investigation into the Ecology, Hydrodynamics, and Limnological Parameters of Oxbow Lakes in the Middle and Lower Savannah River Basin
<b>Project Number:</b>	2015SC98B
<b>Start Date:</b>	3/1/2015
<b>End Date:</b>	2/28/2016
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	SC-003
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	Hydrology, Ecology, Management and Planning
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	John Hains

## Publications

There are no publications.

## Project deliverables

Project deliverables are shown in the Gantt charts below. Funding availability at the beginning of the project and river flooding caused delays in the project so activities are ongoing and will be completed by the end of September 2016.

	March-15	April-15	May-15	June-15	July-15	August-15	September-15	October-15	November-15	December-15	January-16	February-16	March-16
<b>Elevation assessment from historic documents</b>													
Compile information on oxbows													
Assess elevations of oxbow openings													
<b>Hydrologic assessments</b>													
Install water level loggers and peizometers in four oxbows													
Measure general bathymetric parameters													
Monitor and download data													
Analyze hydrologic data													
<b>Chemical dynamics</b>													
Continuously monitor temp., pH, DO, cond in river near oxbows													
Measure temp., pH, DO, cond in river near oxbows													
Measure nutrients in oxbows and river													
<b>Biological dynamics</b>													
Electroshocking in oxbows													
RFID tagging and installation of continuous tag reader in connected oxbow													
Continuous monitoring of RFID tagged fish in connected oxbow													
Macroinvertebrate sampling and identification in oxbows													
Chlorophyll a sampling in oxbows													
<b>Outreach</b>													
Website-monthly updates													
Social media-biweekly updates													
Scientific outreach-SC Water Resources Conference-abstract submittal													
<b>Final report</b>													
Data analysis													
Final report submitted													

	March-15	April-15	May-15	June-15	July-15	August-15	September-15	October-15	November-15	December-15	January-16	February-16	March-16	April-16	May-16	June-16	July-16	August-16	September-16	
<b>Elevation assessment from historic documents</b>																				
Compile information on oxbows																				
Assess elevations of oxbow openings																				
<b>Hydrologic assessments</b>																				
Install water level loggers and peizometers in four oxbows																				
Measure general bathymetric parameters																				
Monitor and download data																				
Analyze hydrologic data																				
<b>Chemical dynamics</b>																				
Continuously monitor temp., pH, DO, cond in river near oxbows																				
Measure temp., pH, DO, cond in river near oxbows																				
Measure nutrients in oxbows and river																				
<b>Biological dynamics</b>																				
Electroshocking in oxbows																				
RFID tagging and installation of continuous tag reader in connected oxbow																				
Continuous monitoring of RFID tagged fish in connected oxbow																				
Macroinvertebrate sampling and identification in oxbows																				
Chlorophyll a sampling in oxbows																				
<b>Outreach</b>																				
Website-monthly updates																				
Social media-biweekly updates																				
Scientific outreach-SC Water Resources Conference-abstract submittal																				
<b>Final report</b>																				
Data analysis																				
Final report submitted																				
<b>Additional work</b>																				
zooplankton sampling																				
Ash Free Dry mass																				

■ original timeline  
■ actual timeline  
■ proposed timeline

**ELEVATION ASSESSMENTS**

<b>Task</b>	<b>Status</b>
Compile information	Partially complete
Ground-truth subset of data	Not complete
Tie oxbow elevation to continuous river elevation	Not complete

**HYDROLOGIC ASSESSMENTS**

<b>Task</b>	<b>Status</b>
Surface water level loggers	Partially complete
Miller Lake	Received 5/11/15; Installed 7/10/15
Whirligig Lake	Received 5/11/15; Installed 7/17/15
Possum Eddy Lake	Received 5/11/15; Installed 9/1/15
Conyers Lake	Received 5/11/15; Installed 7/31/15
Groundwater piezometers	
Miller Lake	Received 5/11/15; Installed 7/17/15
Whirligig Lake	Received 5/11/15; Installed 7/17/15
Possum Eddy Lake	Received 5/11/15; Installed 3/23/16
Conyers Lake	Received 5/11/15; Installed 7/31/15
Data Analysis	
Descriptive Statistics	In progress
Calculate volumetric refresh rates	Not complete

**CHEMICAL DYNAMICS\***

<b>Constituent</b>	<b>Samples Collected</b>	<b>Samples Analyzed</b>
NH3	31	20
NO3	31	19
NO2	31	20
O-phos	31	2
TN	31	15
TP	31	2
TOC	31	15
DOC	31	15
Water Quality Profiles	24	

\*Target was to collect and analyze 16 samples for each constituent (4/year X 4 oxbows)

## BIOLOGICAL DYNAMICS

Task	Status
Fish Sampling (quarterly)	Miller: 7/29/15, 10/27/15, 4/14/16 Whirligig: 7/31/15, 11/6/15, 4/21/16 Possum Eddy: 8/5/15, 4/28/16, fall sample event cancelled due to flooding Conyers: 8/21/15, 4/29/16, fall sample event cancelled due to flooding Unable to perform winter sampling due to flooding
Macroinvertebrate Sampling (quarterly)	Miller: 7/31/15, 10/27/15, 1/29/16, 2/26/16, 3/30/16, 4/28/16, 5/31/16 Whirligig: 7/31/15, 10/27/15, 1/29/16, 2/26/16, 3/30/16, 4/29/16, 5/31/16 Possum Eddy: 8/5/15, 10/28/15, 2/26/16, 3/30/16, 4/28/16, 5/31/16 Conyers: 8/4/15, 10/27/15, 2/29/16, 3/30/16, 4/29/16
Algae via chlorophyll a (quarterly)	Method developed June 2016; all samples will be analyzed July 2016 Miller: 7 samples, 0 analyzed Whirligig: 7 samples, 0 analyzed Possum Eddy: 6 samples, 0 analyzed Conyers: 5 samples, 0 analyzed
Zooplankton*	Miller: 7 samples, 3 analyzed Whirligig: 7 samples, 4 analyzed Possum Eddy: 5 samples, 2 analyzed Conyers: 4 samples, 4 analyzed
RFID Monitoring	Installed RFID antenna and logging system on 5/7/16 Tagged 2 fish on 5/7/16 Will tag more fish during July 2016 fish sampling event

\*Listed under proposal objectives, but not listed in gantt chart or description of project elements

## WEB/SOCIAL MEDIA UPDATES

Task	Status
Website Updates	10/19/2015 - Diatom Project Update: Oxbows 10/14/2015 - Savannah River Oxbow Fish
Social Media	10/21/2015 PCWS Facebook page post 11/16/2015 PCWS Facebook page post 2/29/2016 PCWS Facebook page post 3/20/2015 PCWS Facebook page post 9/4/2015 PCWS Facebook page post 12/17/2015 PCWS Facebook page post 12/7/2015 PCWS Facebook page post 3/23/2015 PCWS Facebook page post 9/14/2015 PCWS Facebook page post 10/29/2015 PCWS Facebook page post

*In-kind contribution*

Phinzy Center leveraged salaries that originated from other non-federal, contract services projects within the Savannah River Basin. The total in-kind requirement for this project is \$53,730; thus far Phinzy has expended \$39,854 with the remainder to be expended by the end of September 2016.

6/26/2016 update

	hours	rate		
Brian	4	\$ 50.00	\$	200.00
Oscar	19.5	\$ 50.00	\$	975.00
Jason	266.2	\$ 37.00	\$	9,849.40
Matt	84.25	\$ 24.00	\$	2,022.00
Katie	294.75	\$ 23.00	\$	6,779.25
Chalisa	265.5	\$ 22.00	\$	5,841.00
Damon	179.4	\$ 22.00	\$	3,946.80
Kelsey	388	\$ 22.00	\$	8,536.00
Liam	96.5	\$ 10.00	\$	965.00
Nikki	60.5	\$ 10.00	\$	605.00
Olivia	13.5	\$ 10.00	\$	135.00
	1672.1			\$39,854.45

# Effect of Climate and Land Use Change on Water Availability for the Savannah River Basin

## Basic Information

<b>Title:</b>	Effect of Climate and Land Use Change on Water Availability for the Savannah River Basin
<b>Project Number:</b>	2015SC99B
<b>Start Date:</b>	3/1/2015
<b>End Date:</b>	2/28/2016
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	SC-003
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	Drought, Surface Water, Climatological Processes
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Ashok Kumar Mishra

## Publications

There are no publications.

# **Effect of Climate and Land Use Change on Water Availability for the Savannah River Basin**

## **1. Introduction**

Fresh water accessibility for human consumption is under threat due to changing climate, limited water supply and growing water demand ( Mishra and Singh, 2010; Vorosmarty et al., 2000). The major source of surface water supply is often complicated due to uncertainty associated with spatio-temporal distribution of rainfall as well as multi-year droughts (Oki and Kanae, 2006). Savannah River Basin (SRB) is a transboundary river basin located in south-east Atlantic region of USA. It has drainage area of 27171 km<sup>2</sup>, out of which 11875 km<sup>2</sup> is located in the South Carolina and 14965 km<sup>2</sup> in Georgia and the remaining portion is located in the state of North Carolina (SCDHEC, 2010). The land cover of SRB consists of forest (69%), agriculture (22%) and urban/developed (7%) areas. The major allocation of water resources in Savannah River includes drinking water (more than 1.5 million people), energy (hydro power generation, nuclear plants etc.), industrial and agricultural water uses (SCDHEC, 2010). The SRB which serves three different states (North Carolina, South Carolina and Georgia) is also likely to be the subject of future trans-boundary disputes caused by climate and land use change as well as growing water demands. During the last decade the SRB was severely affected by extreme droughts that began in early 2006, which in turn dropped reservoir levels faster than any previous drought on record. This situation is only likely to worsen because the water is shared by these three states and each state witness an increase in water scarcity issues. Here we investigated the flow scenario at the SRB by calibrating the Soil and Water Assessment Tool (SWAT).

## **2. Data collection**

### **SWAT input data:**

The basic input data required for setting up the SWAT model are weather data, Hydrography and digital elevation model, Land Use Land Cover (LULC) and soil data.

- i. Weather data: Data needed are precipitation, temperature (minimum and maximum), relative humidity, solar radiation and wind speed. Here we used the station weather data got from NCDC (National Climatic Data Centre)
- ii. Digital Elevation Model: The watershed delineation and topographic parameter estimation is based on the input DEM resolution. USGS provides national elevation

set of all US (<http://ned.usgs.gov/>) with varieties of resolution. We used 30m resolution data as input to the model.

- iii. Land Use Land Cover (LULC): These data is obtained from the Crop Land Data Layer, USDA ([www.nass.usda.gov/research/Crop-land/SARS1a.htm](http://www.nass.usda.gov/research/Crop-land/SARS1a.htm)).
- iv. Soil data: We used SSURGO data, which has high resolution, in the present study.
- v. Stream flow data: The flow data for evaluating the model is obtained from USGS flow gauging stations located at SRB.

### **3. Methodology**

We used Soil and Water Assessment Tool (SWAT) developed by United States Department of Agriculture (USDA), for simulating the flow. The SWAT is a process based, semi-distributed basin scale model (Arnold et al., 1998; Neitsch et al., 2004) and it operates at a daily time step. The model has the advantage to study water quantity (stream flow), water quality (sediment load and nutrients flow) and crop growth in different landscapes and management practices.

Primary requirement of the SWAT model is a Digital Elevation Model (DEM) from which the river basin can be delineated. The delineated river basin is divided to sub-basins, which are further divided in to unique land use/soil/slope units called Hydrologic Response Units (HRUs). Our final model resulted 1408 HRUs distributed over 104 sub-basins. Water balance is the driving force which controls all the process in SWAT model development and the surface runoff is calculated by SCS curve number (CN) method, developed by United State Department of Agriculture (USDA, 1986) natural resource conservation service.

### **4. Results**

Curve number (CN) and available water capacity of the soil layer (Sol\_AWC) were the most sensitive parameter in model parameterization. Index of groundwater flow (Alpha\_BF) also showed high sensitivity. The goodness of fit statistics ( $R^2$ , Nash-Sutcliffe Efficiency (NSE)) was calculated between modeled flow and observed flow, for four hydrologic stations located in the SRB. The time series plot between SWAT stream flow output and USGS stream gauging station 021985000 is presented in Figure 1. The goodness of fit statistics indicates that SWAT model was able to capture the observed stream flow satisfactorily based on  $R^2$  values 0.85 and 0.64 and NSE values 0.76 and 0.58 during model calibration and validation respectively.

## Future work

We will seek to understand how climate change and land use management practices has affected the availability of surface water at the subbasin level within the Savannah River basin.

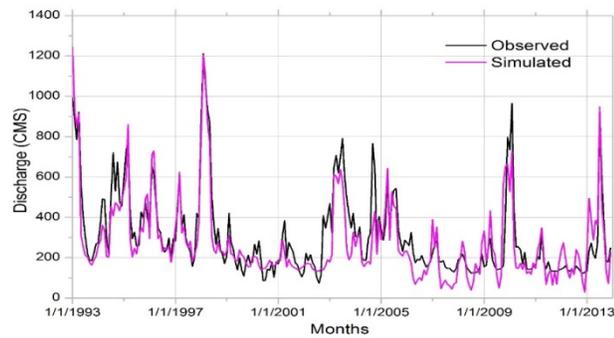


Fig. 1. Time series plot between modeled (SWAT) and observed (USGS) stream flow at gauging station 021985000 at monthly time scale.

## References

- Abbaspour, K.C., 2005. Calibration of hydrologic models: when is a model calibrated? In Zenger, A. and Argent, R.M. (eds) MODSIM 2005 International Congress on Modelling and Simulation. Modelling and Simulation Society of Australia and New Zealand, December 2005, pp. 2449-12455. ISBN: 0-9758400-2-9.
- Arnold, J.G., Srinivasan, R., Muttiah, R.S., Williams, J.R., 1998. Large area hydrologic modeling and assessment part I: Model development1.
- Donner, L. J., et al., 2011: The dynamical core, physical parameterizations, and basic simulation characteristics of the atmospheric component AM3 of the GFDL global coupled model CM3. *Journal of Climate*, 24, 3484–3519
- Dunne, J. P., et al., 2012a: GFDL's ESM2 global coupled climate-carbon Earth System Models. Part II: Carbon system formation and baseline simulation characteristics. *Journal of Climate*, doi:10.1175/JCLI-D-12-00150.1.10/12, in press.
- Dunne, J. P., et al., 2012b: GFDL's ESM2 global coupled climate-carbon Earth System Models Part I: Physical formulation and baseline simulation characteristics. *Journal of Climate*, 25, 6646-6665.
- Golaz, J-C, M Salzmman, Leo J Donner, Larry W Horowitz, Yi Ming, and Ming Zhao, July 2011: Sensitivity of the aerosol indirect effect to subgrid variability in the cloud parameterization of the GFDL Atmosphere General Circulation Model AM3. *Journal of Climate*, 24(13), DOI:10.1175/2010JCLI3945.1.
- Mishra, A.K., Singh, V.P., 2010. A review of drought concepts. *Journal of Hydrology*. 391, 202-216.
- Neitsch, S. L., Arnold, J. G., Kiniry, J. R., and Williams, J. R.: Soil and Water Assessment Tool Input/Output File Documentation Version 2005, Grassland, Soil and water research laboratory Agriculture research services & Black land research Center Texas Agricultural Experiment station, 2004.
- Oki, T., Kanae, S., 2006. Global hydrological cycles and world water resources. *Science*. 313, 1068-1072.
- Salzmman, M, Yi Ming, J-C Golaz, Paul Ginoux, H Morrison, A Gettelman, M Krämer, and Leo J Donner, August 2010: Two-moment bulk stratiform cloud microphysics in the GFDL AM3 GCM: description, evaluation, and sensitivity tests. *Atmospheric Chemistry and Physics*, 10(16), DOI:10.5194/acp-10-8037-2010.
- SCDHEC, 2010. South Carolina Department of Health and Environmental Control, Watershed Water Quality Assessment, [www.scdhec.gov/water](http://www.scdhec.gov/water).
- USDA, S., 1986. Urban hydrology for small watersheds. Technical release. 55, 2-6.
- Vorosmarty, C.J., Green, P., Salisbury, J., Lammers, R.B., 2000. Global water resources: vulnerability from climate change and population growth. *Science*. 289, 284-288.

# Information Transfer Program Introduction

None.

# USGS Summer Intern Program

None.

<b>Student Support</b>					
<b>Category</b>	<b>Section 104 Base Grant</b>	<b>Section 104 NCGP Award</b>	<b>NIWR-USGS Internship</b>	<b>Supplemental Awards</b>	<b>Total</b>
<b>Undergraduate</b>	4	0	0	0	4
<b>Masters</b>	1	0	0	0	1
<b>Ph.D.</b>	1	3	0	0	4
<b>Post-Doc.</b>	0	0	0	0	0
<b>Total</b>	6	3	0	0	9

## Notable Awards and Achievements

Completed funded project for writing the policy and management chapter for the South Carolina Storm-water Pond State of the Knowledge Report

Working on funded project to conduct stakeholder engagement meetings for the SCDNR sponsored South Carolina River Basin Surface Water Assessment. Expect additional funding for groundwater assessment

Completed funded project for a partnership for phase one development of a master plan to the year 2100 for the Greenville, SC Water System. Expect additional funds for phase two implementation plan

Received funding for a project to analyze land use changes and associated water consumption in the Savannah River Basin

Received funding to conduct an economic analysis of changes to flow regimes in the lower Savannah River Basin

Successfully conducted SCWRC statewide research solicitation under the guidelines of USGS.

Served as chairman of the Planning Committee of the S.C. Water Resources Conference

Served on editorial committee for the Journal of South Carolina Water Resources

Co-sponsored second workshop with SC Rural Water Association, American Rivers and SCDHEC on water auditing for municipal water systems.

Continued work to build a partnership for a public/private national technology research center to be housed at Clemson University.

Served on the Savannah River Basin Advisory Council.

Served on the Carolinas Integrated Sciences & Assessments Advisory Board

Served on the SC Sea Grant Consortium Coastal Communities Advisory Board

Served on SCDNR State Water Plan Advisory Committee

Served on the SC Sea Grant Consortium Program Advisory Board

Served on the Science Advisory Committee of the Catawba Wateree Water Management Group

Served on the Selection Committee of the Duke Energy Water Fund

The biennial South Carolina Water Resources Conference (SCWRC) is sponsored by Clemson University Public Service and Agriculture (PSA) and coordinated by the SC Water Resources Center staff, in conjunction with a planning committee made up of statewide water resource professionals. The conference purpose is to provide an integrated forum for discussion of water policies, research projects and water management in order to prepare for and meet the growing challenge of providing water resources to sustain and grow South Carolina's economy, while preserving our natural resources.

In spring 2007, Clemson University first announced that it would establish a biennial conference on water resources in South Carolina to be held in even-numbered years, with the first slated for October 2008. The conference goals are to: (1) communicate new research methods and scientific knowledge; (2) educate scientists, engineers, and water professionals; and (3) disseminate useful information to policy makers, water managers, industry stakeholders, citizen groups, and the general public.

Each of the four previous conferences brought together over 300 registered attendees, featured over 120 presenters and hosted popular plenary speakers. A wider public audience was reached in 2012 and 2014 with live streaming video of the plenary sessions through the conference website. Conference attendees have included those from colleges and universities; municipal water authorities and entities; environmental engineering, consulting and law firms; state and federal agencies; nonprofit organizations; economic development associations; utility companies and land trusts. Participants have responded in an overwhelmingly positive manner about the organization of the conference, the speakers, and the information that has been presented and shared. The conference web site, [www.scwaterconference.org](http://www.scwaterconference.org), provides up to date information for all conference audiences from contributors to presenters and exhibitors and houses the archives for all proceedings to date, including manuscripts and posters. Due to its success and popularity, the conference has become self-sustaining financially.

This year marks the fifth occurrence of the biennial event. The program schedule features four plenary sessions, six tracks, 35 breakout sessions, and 108 oral presentations. The conference will be held at the Columbia Metropolitan Convention Center in Columbia for the fourth year in a row due to its central location in the state and accommodating venue space. In the wake of last year's severe impact on the state's water resources due to drought and flooding, the theme of this year's conference is "SC Water Resources at a Crossroads: Response, Readiness and Recovery".