EFFECTIVENESS OF ENGINEERED AND NATURAL WASTEWATER
TREATMENT PROCESSES FOR THE REMOVAL OF TRACE ORGANICS IN
WATER REUSE

by

Long Cheng

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A Dissertation Submitted to the Faculty of the

DEPARTMENT OF CHEMICAL AND ENVIRONMENTAL ENGINEERING

In Partial Fulfillment of the Requirements

For the Degree of

DOCTOR OF PHILOSOPHY

WITH A MAJOR IN CHEMICAL ENGINEERING

In the Graduate College

THE UNIVERSITY OF ARIZONA

2017

THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

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ACKNOWLEDGEMENTS

It would be very hard for me to appreciate here all the people that have nurtured and helped me during my whole life. However, as I approach to finish my doctorate, the foremost person I need to acknowledge here is my maternal grandpa, who had been inspiring me to be a good man and a educated man since I was a very little kid, and encouraging me to pursue a doctorate after I started my college study. Honestly, I would not even think about getting a Ph.D. without your wisdom and motivation, which have supported and strengthened me through those hard times in last over five years of graduate studies.

I am truly grateful for the consistent encouragement, patient guidance and overall efforts from my advisors Dr. Eduardo Sáez and Dr. Robert Arnold that led me through my Ph.D. study. This long journey would be much tougher without your company indeed. Dr. Scott Huling once told me “Long, you are taking advantage of the best resource of U of A since Bob and Eduardo are your mentors”. He is absolutely right and it is a privilege to have such great opportunity to be the two best professors’ student. Everything I have learnt from you will benefit me for the rest of my life.

I also would like to specially thank Dr. David Quanrud and Dr. Kimberly Ogden for being part of my dissertation committee. I started working with Dr. Quanrud, a brilliant environmental scientist in 2012 and it has been a wonderful experience over these years. Also it is my great pleasure to utilize my fluorescence spectroscopy skills to contribute to the algae study for Dr. Ogden, whose laughter will surely be one of my best memories.

People in my research group have been remarkably helpful and I truly appreciate your assist: Tianqi, Matt, Itzel, Alberto, Hao, Lin, Sarah, Monem and those undergraduate volunteers. I also want to thank Dr. Dominic Gervasio, Dr. Greg Ogden and Dr. Kasi Kiehlbaugh for your support when I was working as a teaching assistant in you courses.

Last but not least, I would like to thank my family for all the love and power you have provided. And also my friends: Bingfeng, Chao, Fanchao, Jianjie, Siqi, Jiaoyang, Margarita, Bing, Ming, Bo, Ruochen and Yan, I cannot image my life here in Tucson without you guys. Thank you! Love you!

In memory of my maternal grandpa, Xinduo Wu

DEDICATION

*To my mom and dad, whose motivation and encouragement over these
years have made this work possible.*

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ABSTRACT

Due to their potential health impact on human beings and ecosystems, persistent trace organic compounds (TOrcs) have aroused concern from both the public and professionals. In particular, the discharge of pharmaceuticals, endocrine disrupters, disinfection byproducts and other TOrcs from wastewater treatment plants into the environment is an area of extensive current research. This work studies the fate and treatments of TOrcs, with emphases on advanced oxidation processes (AOPs).

This work presents predicted removal efficiencies of a variety of engineered and natural processes for 55 frequently encountered TOrcs in treated wastewater, based on previously reported data and using existing predictive models. Correlations between physicochemical and biological properties of TOrcs and treatment performance were explored. Removal of TOrcs in all processes investigated in this study was found to be sensitive to matrix effects. Heuristic guidelines for selection of sequenced treatment processes for TOrcs management were established.

A field reconnaissance of natural process of TOrcs was conducted by analyzing the occurrence and fate of a suite of TOrcs, as well as estrogenic activity in water and sediments in the Santa Cruz River, an effluent-dependent stream in Tucson, Arizona. Some TOrcs, including contributors to estrogenic activity, were rapidly attenuated with distance of travel in the river. TOrcs that have low biodegradability and low octanol-water partitioning coefficients were less removed. Results of independent experiments indicated potential indirect photodegradation of estrogenic compound by reactive species generated from photolysis of effluent organic matter.

Utilizing advanced oxidation processes (AOPs) as tertiary water and wastewater treatment is an option to prevent discharge of TOrCs into the environment. Compared to conventional AOPs, the ability of generating hydroxyl radicals ($\cdot\text{OH}$) without additional doses of hydrogen peroxide (H_2O_2) or ozone makes ultraviolet (UV) photolysis of ferric hydroxo complexes a novel AOP, especially in acidic environments. A $\text{Fe(III)}/\text{UV}_{254}$ kinetic model, which combines Fenton-like mechanism, and photolyses of Fe^{3+} , FeOH^{2+} and H_2O_2 was proposed and experimentally validated to predict Fenton-like and H_2O_2 direct UV_{254} photolysis scenarios, individually. Nevertheless, the model underestimated the ferrous ion development during $\text{Fe(III)}/\text{UV}_{254}$ photolysis, perhaps due to the over-prediction of the oxidation of Fe^{2+} by $\cdot\text{OH}$.

The $\text{UV}/\text{H}_2\text{O}_2$ AOP was also studied in this work. A predictive kinetic model was developed to evaluate process efficiency of oxidation of *p*-cresol by $\text{UV}/\text{H}_2\text{O}_2$ photolysis based on a complete reaction mechanism, including reactions of intermediates with $\cdot\text{OH}$. Results of this study highlight the significance of consideration of radical scavenging effects by the byproducts from oxidation of organic matter in model prediction performance.

CHAPTER 1: Introduction

Due to human overpopulation and water pollution, water scarcity is becoming a more and more serious global environmental issue, especially in arid and semi-arid regions (Watkins 2006). Water reclamation, including direct and indirect portable reuse of treated wastewater, has been proposed as a sustainable method to preserve water resources in order to meet commercial, industrial and drinking water supply needs (Ahuja 2014; Becerra-Castro et al. 2015; Thomure and Kmiec 2015). However, conventionally treated municipal wastewater (secondary effluent) usually contains an assortment of sub-part-per-billion (ppb) levels of dissolved organic matter (DOM), such as pharmaceuticals and personal care products (PPCPs), endocrine disrupting chemicals (EDCs), disinfection by-products (DBPs), flame retardants, pesticides and insecticides (e.g. Miège et al. 2009; Wen et al. 2009; Rojas et al. 2013; U.S. EPA 2010).

Wastewater treatment facility (WWTF) removal efficiencies during secondary treatment were summarized for 180 trace organic compounds (TOrcs) as functions of temperature, solids retention time (SRT), and hydraulic retention time (HRT) by Miège et al. (2009). Compounds that were, on average, efficiently removed (> 90%) included the natural estrogens, 17- β estradiol and estriol; propranolol; salicylic acid; and paracetamol, among others. On the other hand, atenolol, carbamazepine and metoprolol generally exhibited poor removal efficiencies (< 10%). The study pointed out that up to 40% of observed (average) TOrc removals occurred during primary treatment, and 50-90% of the overall reduction was a consequence of activated sludge treatment, although the contributions of solid-phase partitioning and chemical transformation were not assessed individually. Nutrient removal processes proved particularly useful in lowering the concentrations of

most TOrCs. Process-dependent removals of 42 prominent TOrCs including PPCPs, alkylphenols, pesticides, plasticizers, and others during conventional wastewater treatment were statistically analyzed by Rojas et al. (2013). Hydrophobicity and biodegradability (as quantified by BioWin models and laboratory-scale experiments) were, as expected, the most important compound properties affecting TOrC removal rates in WWTFs. Similar to the observations of Miège et al. (2009), hormones such as testosterone and estrogenic compounds were good targets for conventional processes, with removal efficiencies typically greater than 75%. Carbamazepine and perfluorinated compounds (PFOA and PFOS), however, are exceptionally resistant to conventional treatment processes. The great variation in reported data related to the removal of antibiotics suggests that treatment efficiencies for these compounds are sensitive to operating conditions, which sometimes go unreported. The same lack of supporting information tends to obscure cause-effect relationships among compound characteristics, process parameters and removal efficiencies.

The occurrence and fate of xenobiotic TOrCs in the environment have been widely and intensively investigated for decades (e.g. Lye et al. 1999; Soares et al. 2008; Pal et al. 2010) due to their potential threat to human and ecosystems, as suggested by Colborn et al. (1996). Results of a nationwide reconnaissance on concentrations of 95 TOrCs in 139 U.S. surface waters were reported by Kolpin et al. (2002). More than 85% of the 95 target contaminants were detected at one or more sampling sites. Presence of TOrCs in groundwater was reviewed by Lapworth et al. (2012) and Sui et al. (2015). Although many of the TOrCs pose no human health risk at the concentrations reported in those surveys, some, most notably hormones and hormone mimics, have proven capable of

feminizing continuously exposed male fish and other organisms at the concentrations encountered (Purdom et al. 1994; Sumpter 1995; Kidd et al. 2007).

Natural attenuation of TOrCs in surface water has been widely reported (Boreen et al. 2003; Fono et al. 2006; Leech et al. 2009). Aside from sediments adsorption and biodegradation, photochemical degradation pathways are believed to be contributing factors to TOrC attenuation. In general, photo-transformations of TOrCs can be attributed to two mechanisms: direct photolysis and indirect photolysis. Direct photolysis involves chemical bond cleavage after susceptible compounds absorb photons of specific energy levels. Some DOMs and inorganic matter can produce transient reactive species that can attack themselves as well as other TOrCs, leading to indirect photolysis (Cooper et al. 1988). Indirect photolysis has been investigated based on three main mechanisms: (1) production of reactive oxygen species (ROS), such as hydroxyl radical ($\cdot\text{OH}$) (Carlos et al. 2012; Lee et al. 2013) and singlet oxygen ($^1\text{O}_2$) (Mostafa and Rosario-Ortiz 2013), (2) reactive inorganic radicals like carbonate radicals ($\text{CO}_3^{\cdot-}$) (Jasper and Sedlak 2013), and (3), photo-excited (i.e.—triplet state) DOM intermediates (Rosario-Ortiz and Canonica 2016).

Advanced oxidation processes (AOPs), which utilize $\cdot\text{OH}$ to destroy TOrCs, have been extensively studied in both academia and industry (e.g. Rosario-Ortiz et al. 2010; Matilainen and Sillanpää 2010; Rodríguez et al. 2012; Prieto-Rodríguez et al. 2013; Pešoutová et al. 2014). Due to its $\cdot\text{OH}$ generation ability without input of hydrogen peroxide (H_2O_2) or ozone (O_3), ferric hydroxo complexes ultraviolet (UV) photolysis is an attractive AOP. Numerous studies of TOrCs removals using Fe(III)/UV photolysis have been reported (e.g. Andreozzi et al. 2006; Rodríguez et al. 2007; Jin et al. 2014).

The fundamental kinetic mechanism of such photolysis process is however, relatively less investigated. A basic Fe(III)/UV photolysis mechanism was proposed by Baxendale and Magee (1955). Studies conducted afterwards to understand the process mostly reported quantum yields under various experimental conditions (e.g.—temperature and irradiation source) by using $\cdot\text{OH}$ scavengers in short term irradiation experiments to avoid oxidation of Fe(II) by $\cdot\text{OH}$ (e.g. Logan 1990; Kawaguchi and Inagaki 1993; Joseph et al. 2001; Rodríguez et al. 2002; Lee and Yoon 2004). Very few studies (Machulek et al. 2009; Wang and Liu 2014) have focused on developing a kinetic model that combines Fe(III)/UV photolysis and relevant iron and radical reactions to simulate such photolysis process in the absence of additional added $\cdot\text{OH}$ scavengers on a long term scale.

The UV/H₂O₂ photolysis process has been one of the most studied AOPs. Three common elements are usually employed in the development of quantitative models for the process: (i) photo-generation of $\cdot\text{OH}$ from the direct photolysis of H₂O₂ and $\cdot\text{OH}$ quenching by H₂O₂ and other radicals; (ii) oxidation of the target compound by $\cdot\text{OH}$; and (iii), $\cdot\text{OH}$ scavenging by oxidation byproducts (Lay 1989; Glaze et al. 1995; Liao and Gurol 1995; Stefan et al. 1996; Crittenden et al. 1999; Murcia et al. 2015; Rojas et al. 2010, 2011). Although the complete chemistry of the process, including radical-radical reactions are taken into account in kinetic models, the impact of presence of intermediate from oxidation of target organics has been rarely considered.

This dissertation has a general objective to investigate and quantify the engineered and natural treatment processes of municipal wastewater to degrade TOxCs for water reuse purpose. To emphasize the relevance of the research, this work has included a comprehensive modeling analysis of the removal efficiencies of conventional/secondary

and tertiary wastewater treatment technologies as well as natural process for 55 frequently encountered TOrCs based on reported compound-dependent physicochemical properties and currently available modeling tools. As a key component of this research, a field study of occurrence and fate of TOrCs in a wastewater effluent dependent river to assess the effectiveness of natural attenuation is presented in later chapter. In addition, this dissertation has documented projects of two different UV-driven AOPs, Fe(III)/UV₂₅₄ photolysis and UV/H₂O₂ photolysis that were investigated from development of kinetic mechanism and consideration of intermediates impact perspectives respectively, for future better evaluation of treatment technologies for TOrCs removal applications.

For general information purposes, a brief description of each of the chapters along with the author's contribution is provided below:

APPENDIX A: Effectiveness of Engineered and Natural Wastewater Treatment Processes for the Removal of Trace Organics in Water Reuse

In this work, the physicochemical and biological determinants of 55 TOrCs removal efficiencies in a variety of engineered and natural processes were explored via extensive modelling on previously reported data and using existing model/software. Heuristic guidelines for process selection were established based on this information. The treatment processes considered include conventional wastewater treatment (biological), tertiary treatment such as AOP, reverse osmosis (RO) and granular activated carbon (GAC), and natural process, i.e.—sunlight photolysis.

The author of this dissertation performed the target TOrCs selection, literature review of physicochemical properties of the 55 TOrCs, biodegradability prediction, AOP and GAC processes modeling and data analysis and led the writing for the publication.

APPENDIX B: Fate of Trace Organics in a Wastewater Effluent Dependent Stream

In this work, concentrations of selected TOrCs and estrogenic activity in surface water, ground water and riverbed sediments samples collected along lower Santa Cruz River, Tucson, Arizona, were determined in order to investigate fate of trace organics in a wastewater effluent dependent stream. Some TOrCs along with estrogenic activity were found to attenuate rapidly with river travel distance. TOrCs with low biodegradability and low octanol-water partitioning coefficient were less degraded. Natural attenuation of estrogenic compounds in treated wastewater was attributed to indirect sunlight photo-degradation mechanisms, based on results of independent study.

The author of this dissertation prepared the sampling plan, participated in four river sampling campaigns, performed sample preparations, including filtration and microwave extraction, analyzed total suspended solids, conducted fluorescence spectroscopy study using excitation-emission matrix (EEM) analysis, executed independent experiment to explore potential mechanisms of estrogenic compound natural attenuation, including modeling ground level solar spectral irradiance and provided writing assistance for the section “Phototransformation effects” in the publication.

APPENDIX C: Photolysis of Fe(III) Hydroxo Complexes in Aqueous Solutions

In this work, a kinetic model of Fe^{3+} and FeOH^{2+} photolysis combined with Fenton-like mechanism was proposed to study the kinetics of Fe(III)/UV photolysis in the absence of

additional $\cdot\text{OH}$ scavengers on a long term scale. The established model was proven capable of simulating Fenton-like and UV/H₂O₂ photolysis. Nevertheless, the model overestimated Fe(II) accumulation when Fe(ClO₄)₃ solutions were irradiated by UV₂₅₄. Further investigation indicated that failure of the model to predict Fe(III)/UV photolysis is due to overestimation of oxidation of Fe²⁺ by $\cdot\text{OH}$. The modeling performance improved when Fe(ClO₄)₃ solutions were irradiated with presence of H₂O₂ and/or Fe(II).

The author of this dissertation proposed the kinetic mechanism, designed and built experimental setup, performed modeling and experimental studies as well as data analysis and led the writing of the manuscript.

APPENDIX D: Modeling the Oxidation of Phenolic Compounds by Hydrogen Peroxide Photolysis

In this work, a $\cdot\text{OH}$ radical reaction pathway based on phenol's degradation mechanism was proposed and validated to investigate the degradation of *p*-cresol during UV/H₂O₂ photolysis in a well-mixed batch reactor. Reaction rate constants, ionic strength changes and pH changes of the solution were considered. In addition, quantum yield of *p*-cresol direct photolysis under UV₂₅₄ irradiation was also determined. Target compound removal efficiency as well as the impact of presence of reaction intermediates under various experimental conditions was predicted using the proposed kinetic model.

The author of this dissertation led incorporating the reaction byproducts on accurate model prediction, designed and built experimental setup, established the first version of the kinetic model, and performed experimental studies.

CHAPTER 2: Conclusions

The idea proposed by Grady that, in most engineering applications, transformations of multiple xenobiotic compounds could be treated independently, using a single-substrate kinetic approach stimulated our study in which predicted removal efficiencies of 55 selected TOrCs were individually investigated in a single-substrate—i.e. a representative treated wastewater, during engineered (conventional and tertiary treatments) and natural (sunlight direct photolysis) processes using currently available data and modeling tools. It is clear that simply applying QSAR estimated biodegradability to predict overall liquid phase TOrCs removals during conventional wastewater treatment is not absolutely reliable, which confirms previously reported observations. All tertiary treatments investigated in this study are capable of attenuating a broad spectrum of TOrCs. Their removal efficiencies are however sensitive to compound-related physicochemical properties as well as background organic matter present in the water matrix. Removals were predicted without considering the potential impact from reaction intermediates and interactions among background matter with target TOrCs and intermediates due to lack of good understanding of matrix effects as well as degradation mechanism of TOrCs during UV based tertiary treatment and sunlight photolysis. Radical quenching and light screening effects of matrix compounds can significantly impair TOrCs treatment efficiency. Qualitative and quantitative understanding of matrix interferences both in terms of physical (e.g. light shading) and chemical (such as degradation mechanisms, radical scavenging and production of reactive species) effects remains a key challenge in the simulation of treatment technologies.

It is apparent that some TOrCs, including compounds with high biodegradability and those that contribute to estrogenic activity, are rapidly attenuated with distance of travel in a wastewater effluent-dependent river. Independent experiment results suggest that the degradation of estrogenic compounds is attributed, at least in part, to indirect photolysis caused by reactive species which are generated from sunlight photo-transformation of EfOM. This attenuation mechanism is believed to play an important role in fate of TOrCs in surface waters. In general, TOrCs that survive percolation to groundwater have low biodegradability and low octanol–water partitioning coefficient. Data suggest that concentrations of hydrophobic TOrCs in riverbed sediment are periodically affected by storm-related scouring during periods of heavy rainfall and runoff. Our results indicate that fate of TOrCs in a treated wastewater-impacted river can be affected by the resuspension and transport of sediments. Given the overall evidence gathered from this field study, potential economical treatment for TOrCs-contaminated surface and groundwater remediation based on such natural purification process can be exploited.

A kinetic model that consists of Fenton-like system and UV_{254} photolyses of Fe^{3+} , FeOH^{2+} and H_2O_2 based on literature results and physicochemical data was proposed to predict Fe(II) behavior during $\text{Fe}(\text{ClO}_4)_3/\text{HClO}_4$ UV_{254} photolysis in the absence of additional $\cdot\text{OH}$ scavengers under a wide range of operating conditions on a long term scale. Good agreement between experimental and predicted results indicates that the model is capable of forecasting H_2O_2 decomposition in both Fenton-like and $\text{UV}/\text{H}_2\text{O}_2$ photolysis scenarios. Calculated spectra of $\text{Fe}(\text{ClO}_4)_3$ solutions with different total iron concentrations and pH are a match with experimentally measured spectra, which proves the validity of solution speciation prediction as well as molar absorptivity information of

light absorbing compounds. Values of reported Φ_{Fe} and Φ_{FeOH} were also verified via short term irradiation experiments using excess *p*-cresol as $\cdot\text{OH}$ scavenger. Nevertheless, measured Fe(II) concentrations are much higher than predicted levels. Further modeling study results suggest that such unexpected error is caused by overestimation of Fe^{2+} oxidation by $\cdot\text{OH}$, which leads to two possible hypotheses: (i) significant $\cdot\text{OH}$ scavenging by unknown species, and/or (ii) a “shielding” effect on Fe^{2+} which keeps $\cdot\text{OH}$ from reacting with Fe^{2+} in first few minutes of the process. It is appealing that prediction accuracy can be improved when $\text{Fe}(\text{ClO}_4)_3$ solutions are irradiated in the presence of H_2O_2 and/or Fe(II).

A kinetic model considering $\cdot\text{OH}$ reactions with oxidation process intermediates was developed to predict the degradation of *p*-cresol by UV/ H_2O_2 AOP in a well-mixed batch reactor. The model was established based on known elementary chemical and photochemical reactions of the UV/ H_2O_2 photolysis system, combined with experimentally established direct photolysis reactions and proposed mechanism of reactions of oxidation byproducts with $\cdot\text{OH}$. The behavior of *p*-cresol attenuation, as well as the major oxidation intermediates (4-methylcatechol), was successfully simulated under various experimental conditions. Taken together, results well indicate the importance of considering full reaction mechanism which includes potential impact due to the presence of intermediates to lead reliable process evaluation.

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**APPENDIX A: Effectiveness of Engineered and Natural Wastewater Treatment
Processes for the Removal of Trace Organics in Water Reuse**

This article was published in Journal of Environmental Engineering (2017)

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Abstract

The physicochemical and biological determinants of removal efficiencies in a variety of engineered and natural processes were explored for 55 frequently encountered trace organic compounds (TOrcs) in wastewater. Weak correlations between field observations and predicted TOrc biodegradabilities led to adoption of an empirical approach to prediction of compound removal during conventional wastewater treatment. The efficiencies of TOrc removals by UV photolysis (direct and indirect), activated carbon adsorption, membrane separation (reverse osmosis/nanofiltration) and sunlight photolysis were determined under representative process conditions. Results led to heuristic guidelines for the selection of sequenced treatment processes for TOrc management. Process- and compound-specific treatment efficiencies were sensitive to TOrc physicochemical properties and matrix effects.

Keywords: trace organic compounds; tertiary wastewater treatment; advanced oxidation process; photolysis; biotransformation.

A.1 Introduction

Population growth and drought have produced unprecedented stress on regional water resources, especially in arid and semi-arid regions. Potable reuse of treated wastewater is a potential remedy but is impeded in part by the persistence of trace organics in conventionally treated wastewaters. A number of such compounds are poorly attenuated during conventional wastewater treatment (Jones et al. 2005; Miège et al. 2009; U.S. Environmental Protection Agency (EPA) 2009; 2010), so that a combination of conventional and advanced processes is necessary to restore water to potable quality.

Grady (1990) provided a pragmatic approach to rational, engineered biotransformations of xenobiotic organic compounds during conventional wastewater treatment. The article highlighted the difficulties inherent in simulating diverse, mixed-culture treatment of trace organics in the presence of a primary substrate. Citing extant kinetic and reactor performance data, Grady suggested a pathway for closing related gaps in process design and operation.

Grady emphasized the roles of available tools in reactor engineering, such as manipulation of solids and hydraulic retention times under aerobic, anaerobic and anoxic conditions, acknowledging that development of relationships between operational parameters and attenuation of trace organics remained a work in progress. Missing, at least in part, were databases necessary to determine intrinsic kinetic parameters, positive and negative interactions among substrates during biological treatment and the potential importance of non-biological removal mechanisms (volatilization and adsorption).

To simplify the problem, Grady suggested that all wastewater substrates could be lumped into three components—biogenic, toxic and individual target compounds. Targets were selected based on persistence and toxicity. To be useful, each compartment must be measureable—e.g., biogenic organics as total organic carbon—highlighting the importance of advanced analytical chemistry. Absent simplifications of this nature, successful process simulation was unlikely or impossible. Instead, Grady used Monod kinetics and its several rational extensions, accounting for observable positive (co-metabolic) and negative (toxicity) biochemical interactions. Grady laid out the limitations and strengths of the Andrews equation, for example, in process simulations, identifying information necessary to simulate the biodegradation of xenobiotic contaminants during conventional wastewater treatment and also proposing a reasonable set of steps to acquire missing data.

Grady's article covered many cases in which multiple xenobiotic compounds were simultaneously present—the rule in municipal wastewater treatment. The main conclusion was that in most engineering applications, transformations of multiple xenobiotic compounds could be treated independently, using a single-substrate kinetic approach. Grady was among those early to recognize that removal efficiency of xenobiotic compounds in continuous culture can be greatly enhanced by the presence of multiple biogenic compounds through co-metabolism.

A simplification was recommended for dealing with microbial community complexity and substrate specificity in mixed cultures. Grady reasoned that the fraction of cells degrading each target xenobiotic compound was proportional to the compound's contribution to chemical oxygen demand. Under those conditions, the total biomass could

be separated into the fraction that degrades the target compound and the fraction that degrades everything else. Grady also identified the tools necessary to anticipate the fates of xenobiotic compounds in complex media, accounting for inter-phase partitioning, specific biotransformation rates and biomass. These included structure/activity relationships in various reactor configurations—e.g., activated sludge, trickling filters. Grady suggested that life scientists and environmental engineers should collaborate to establish the potential and role of biotechnology in protection of environmental and human health, accelerating the development of knowledge regarding the fates of xenobiotic contaminants during municipal wastewater treatment and following their discharge into the environment.

A relative few works so usefully stimulate broad-scale thinking relative to substantial environmental engineering problems as Grady's 1990 article. It was a departure point for much of the engineering effort aimed at treatment of trace organic contaminants in wastewater—an area that has gained attention with progress in analytical chemistry and toxicology.

The requirement for at least secondary treatment remains a foundation of municipal wastewater treatment. Unfortunately, conventional wastewater treatment is only partially successful in removing trace organics, including those that affect environmental and human health. At the same time, stress on existing water resources necessitates consideration of waters of initially low quality in water resources planning—to the point at which direct potable reuse of treated wastewater is sometimes considered seriously. Persistent trace organics impede such plans. There are neither universally accepted

standards of treatment for many such compounds nor levels of exposure that are recognized as safe (Maruya et al. 2014).

The term trace organic compounds (TOrcs) is used to represent pharmaceuticals and personal care products (PPCPs), endocrine disrupting compounds (EDCs), disinfection by-products (DBPs), flame retardants, insecticides and herbicides and an assortment of additional organic compounds that are recognizable in water at sub-part-per-billion (ppb) levels. Public interest in TOrcs was enormously stimulated by Colborn et al. (1996), who informed on the potential threats to human health from man-made chemicals in water. In an unprecedented survey, Kolpin et al. (2002) reported the concentrations of 95 TOrcs in 139 U.S. surface waters. More than 85% of the 95 analytes were present at one or more sites. The influence of that study on the trajectory of environmental science is well illustrated by the frequency with which it has been cited—a total of 3911 times by July 2016, according to Web of Science. More recently, Lapworth et al. (2012) and Sui et al. (2015) reviewed presence of TOrcs in ground waters. Although many of the TOrcs in these surveys pose no currently recognizable human or ecological health risk, some cause physiological changes in exposed organisms at the concentrations encountered (Purdum et al. 1994; Sumpter 1995; Kidd et al. 2007).

There has been considerable recent effort to establish the fate of TOrcs during municipal wastewater treatment (e.g. Jones et al. 2007; Daughton and Ternes 1999; Urase and Kikuta 2005; Rojas et al. 2013). Eighty-eight studies involving almost 600 treatment systems carried out during 2003-2008 were summarized by the U.S. EPA (2010) to consolidate a database for more than 200 TOrcs. That work provides an accessible tool with which to anticipate TOrc removals by various treatment processes in different water

matrices. Mean removal efficiencies and relative standard deviations during secondary treatment were summarized for 184 TOrCs as functions of temperature, solids retention time (SRT) and hydraulic retention time (HRT) by Miège et al. (2009). Compounds that were, on average, efficiently removed ($> 90\%$) included the natural estrogens, 17β -estradiol and estriol, propranolol, salicylic acid, and paracetamol, among others. On the other hand, atenolol, carbamazepine and metoprolol exhibited poor removal efficiencies ($< 10\%$). Up to 40% of observed (average) TOrC removals occurred during primary treatment, and 50-90% of the overall reduction was a consequence of activated sludge treatment, although the contributions of solid-phase partitioning and biotransformation were not separated.

Process-dependent removals of 42 prominent TOrCs including PPCPs, alkylphenols, pesticides and plasticizers during conventional wastewater treatment were statistically analyzed by Rojas et al. (2013). Hydrophobicity and biodegradability (as quantified by BioWin models and laboratory-scale experiments) were, as expected, the most important compound properties affecting TOrC removal efficiencies. Similar to the observations of Miège et al. (2009), hormones such as testosterone and estrogens were good targets for conventional processes, with removal efficiencies typically greater than 75%. Carbamazepine and perfluorinated compounds (PFOA and PFOS), however, were exceptionally resistant to conventional treatment. The great variation in reported removals of individual antibiotics suggests that treatment efficiencies for these compounds are sensitive to operating conditions. Unfortunately, the lack of supporting information tends to obscure cause-effect relationships among compound characteristics, process parameters and removal efficiencies.

In this work, we explore the physicochemical and biological determinants of TOrC removal efficiencies in a variety of engineered and natural processes. Specific objectives are to: (i) examine currently available methods for predicting TOrC biodegradation during conventional treatment; (ii) test potential relationships among biodegradability, compound hydrophobicity and the kinetics of specific physicochemical transformation processes, such as oxidation by hydroxyl radicals ($\cdot\text{OH}$) and photolysis; and (iii) examine the utility of physicochemical processes as bases for tertiary treatment of TOrCs. This information can lead to heuristic guidelines for process selection. The treatment processes considered include (i) biodegradation, (ii) chemical transformations (direct and indirect photolysis, advanced oxidation), and (iii) separation processes (reverse osmosis (RO)/nanofiltration (NF) and activated carbon adsorption).

A.2 Methods

A.2.1 TOrC Selection Criteria

Candidate TOrCs included PPCPs, hormones and hormone mimics, herbicides and insecticides, polycyclic aromatic hydrocarbons (PAHs), plasticizers, alkylphenols and other trace contaminants that are commonly encountered in municipal wastewater. A set of 55 TOrCs was selected that (i) differ in terms of their susceptibility to removal during conventional secondary wastewater treatment (Miège et al. 2009; Rojas et al. 2013), (ii) are detected with $> 20\%$ frequency in surface and ground waters that are influenced by the discharge of treated wastewater (Kolpin et al. 2002; Sui et al. 2015), and (iii) have been the subject of widespread interest in previous studies (Comerton et al. 2008; Rivas

et al. 2011; Wols and Hofman-Caris 2012). Compound-specific characteristics are presented in Table A-1.

A.2.2 Physicochemical Properties

In addition to Estimation Programs Interface (EPI) SuiteTM (v4.11) from U.S. EPA (2016) and PhysChem Module in ACD/Labs Percepta Platform, over 140 literature sources were reviewed for relevant data. The resultant database covers (i) basic information such as molecular weight, octanol/water partition coefficient (K_{ow}) and pKa values; (ii) photochemical parameters such as molar absorptivity and quantum yields; (iii) $\cdot OH$ reaction rate constants; (iv) physical parameters such as molar volume, water solubility and Freundlich constants; and (v) 3-D molecular structure and molecule dimensions (theoretical molecular length and thickness). The K_{ow} information was obtained from the EPI SuiteTM database unless otherwise indicated. Estimated pKa values were taken from 11 different sources (Table A-1). The pH-dependent octanol-water distribution coefficient (D_{ow}) was calculated at pH 7 using:

$$D_{ow} = K_{ow} \frac{1 + 10^{-pKa}}{1 + 10^{pH-pKa}} \quad \text{Eq (A-1)}$$

Table A-1. List of the 55 TOrCs selected for this study, including octanol-water partition coefficients (K_{ow}) and pK_a , reported at ambient or near-ambient conditions.

TOrCs	TOrC ID	CAS Number	Molecular Weight	General Class	log K_{ow}	pK_a
1,4-Dichlorobenzene (1,4-DCB)	1	106-46-7	147.00	Deodorizer	3.44	—
17a-Ethynyl estradiol (EE ₂)	26	57-63-6	296.41	Hormone	3.67	10.3 ^b
17b-Estradiol (E ₂)	24	50-28-2	272.39	Hormone	4.01	10.3 ^b
2,4-Dichlorophenoxyacetic acid (2,4-D)	2	94-75-7	221.04	Herbicide	2.81	2.6 ^e
Acetaminophen	3	103-90-2	151.17	Antipyretic	0.46	9.5 ^b
Anthracene	4	120-12-7	178.24	PAH	4.45	—
Atrazine	5	1912-24-9	215.69	Herbicide	2.61	3.2 ^b
Benzo(a)pyrene	6	50-32-8	252.32	PAH	6.13	—
Benzophenone	7	119-61-9	182.22	UV blocker	3.18	—
Bezafibrate	8	41859-67-0	361.83	Lipid regulator	4.25 ^a	3.6 ^c
Bisphenol A	9	80-05-7	228.29	Plasticizer	3.32	9.8 ^b
Bromoxynil	10	1689-84-5	276.92	Herbicide	3.39 ^a	4.1 ^f
Caffeine	11	58-08-2	194.19	Stimulant	-0.07	-0.92 ^b
Carbamazepine	12	298-46-4	236.28	Anti-epileptic	2.45	16.0 ^b
Carbofuran	13	1563-66-2	221.26	Pesticide	2.32	12.3 ^g
Chlorpyrifos	14	2921-88-2	350.59	Insecticide	4.96	—
Ciprofloxacin	15	85721-33-1	331.35	Antibiotic	0.28	6.1 ^c
Clofibric acid	16	882-09-7	214.65	Metabolite	2.57	2.8 ^c
Diazinon	18	333-41-5	304.35	Insecticide	3.81	2.4 ^h
Diclofenac	19	15307-86-5	296.15	Anti-inflammatory	4.51	4.0 ^b
Diphenhydramine	20	58-73-1	255.36	Antihistamine	3.27	9.0 ^d
Diuron	21	330-54-1	233.10	Herbicide	2.68	—
Doxycycline	22	564-25-0	444.44	Antibiotic	-0.02	—
Estriol (E ₃)	25	50-27-1	288.39	Hormone	2.45	10.3 ^b
Estrone (E ₁)	23	53-16-7	270.37	Hormone	3.13	10.3 ^b

Table A-1. (Continued).

TOrCs	TOrC ID	CAS Number	Molecular Weight	General Class	log K _{ow}	pKa
Fluoranthene	27	206-44-0	202.26	Various	5.16	—
Gemfibrozil	28	25812-30-0	250.34	Lipid regulator	4.77 ^a	4.4 ^b
Ibuprofen	29	15687-27-1	206.29	Anti-inflammatory	3.97	4.9 ^b
Indomethacin	30	53-86-1	357.80	Anti-inflammatory	4.27	4.5 ^c
Iopromide	31	73334-07-3	791.12	Contrast medium	-2.05	—
Ketoprofen	32	22071-15-4	254.29	Anti-inflammatory	3.12	4.5 ^c
Linuron	33	330-55-2	249.10	Herbicide	3.2	—
MCPA	34	94-74-6	200.62	Herbicide	3.25	3.1 ⁱ
Mefenamic acid	35	61-68-7	241.29	Anti-inflammatory	5.12	—
Metolachlor	36	51218-45-2	283.80	Herbicide	2.9	—
Metoprolol	37	51384-51-1	267.37	Betablocker	1.88	9.6 ^d
N,N-Diethyl-toluamide (DEET)	17	134-62-3	191.28	Insecticide	2.18	—
Naproxen	38	22204-53-1	230.27	Anti-inflammatory	3.18	4.2 ^b
Nonylphenol	39	25154-52-3	220.36	Detergent metabolite	5.76	10.3 ^c
Norfloxacin	40	70458-96-7	319.34	Antibiotic	-1.03	6.3 ^d
Octylphenol	41	1806-26-4	206.33	Detergent metabolite	5.5	9.9 ^c
Phenanthrene	42	85-01-8	178.24	PAH	4.46	—
Phenol	43	108-95-2	94.110	Disinfectant	1.46	9.9 ^j
Progesterone	44	57-83-0	314.47	Hormone	3.87	19.3 ^k
Propachlor	45	1918-16-7	211.69	Herbicide	2.18	—
Pyrene	46	129-00-0	202.26	PAH	4.88	—
Ranitidine	47	66357-35-5	314.41	Antacid	0.27	2.7 ^c
Roxithromycin	48	80214-83-1	837.07	Antibiotic	2.75 ^a	9.0 ^c
Simazine	49	122-34-9	201.66	Herbicide	2.18	1.6 ^l
Sulfamerazine	50	127-79-7	264.30	Antibiotic	0.14	7.4 ^c
Sulfamethoxazole	51	723-46-6	253.28	Antibiotic	0.89	6.2 ^b

Table A-1. (Continued).

TOrCs	TOrC ID	CAS Number	Molecular Weight	General Class	log K _{ow}	pKa
Testosterone	52	58-22-0	288.43	Hormone	3.32	19.4 ^b
Tetracycline	53	60-54-8	444.44	Antibiotic	-1.3	3.3 ^c
Triclosan	54	3380-34-5	289.55	Disinfectant	4.76	8.1 ^c
Trimethoprim	55	738-70-5	290.32	Antibiotic	0.91	7.2 ^b

^a K_{ow} values were estimated by KOWWIN program in the EPI SuiteTM.

^b pKa data from Stevens-Garmon et al. (2011).

^c pKa data from Rojas et al. (2013).

^d pKa data from Petrović and Barceló (2007).

^e pKa data from Celis et al. (1999).

^f pKa data from Carpenter et al. (1964).

^g pKa data from Knaak et al. (2008).

^h pKa data from Ku et al. (1998).

ⁱ pKa data from Hiller et al. (2006).

^j pKa data from Brown et al. (2011).

^k pKa data from Li et al. (2013).

^l pKa data from Senseman (2007).

Photochemical parameters are listed in Table A-2. When multiple values were reported, means and standard deviations are provided. Table A-3 contains a summary of parameters required by Adsorption Design Software (AdDesignSTM), which was utilized to compare carbon adsorption capabilities for selected TOrCs. Unless stated otherwise, molar volumes were estimated using PhysChem Module, and boiling points were predicted using EPI SuiteTM. Water solubilities and vapor pressures are from EPI SuiteTM. Freundlich isotherm parameters are from various literature sources.

Three-dimensional molecular structures were created and optimized using the software package Materials Studio 4.0. Theoretical molecular length was defined as the maximum distance between any two atoms in a single compound. Molecular thickness was calculated as the maximum distance between any two atoms in the compound on planes perpendicular to the direction of theoretical molecular length. Examples of the data are shown in Table A-4 and Figures A1-1 to A1-10. These geometrical parameters were used to correlate membrane rejections for each compound.

Table A-2. Photochemical properties (quantum yield at 254 nm, $\Phi_{\text{TOrc-254}}$, molar absorptivity at 254 nm, $\epsilon_{\text{TOrc-254}}$, and reaction rate constant with $\cdot\text{OH}$, $k_{\text{TOrc}\cdot\text{OH}}$) for the 55 TOrcs in this study. Properties are reported at ambient or near-ambient conditions. An expanded version of this table with corresponding sources is presented in Tables A1-1 and A1-2.

TOrcs	$\Phi_{\text{TOrc-254}}$ $\times 10^{-2}$ mol/Ein	$\epsilon_{\text{TOrc-254}}$ $\times 10^3 \text{ M}^{-1}\text{cm}^{-1}$	$k_{\text{TOrc}\cdot\text{OH}}$ $\times 10^9 \text{ M}^{-1}\text{s}^{-1}$	$\Phi_{\text{TOrc-sunlight}}$ $\times 10^{-2}$ mol/Ein
1,4-DCB	60.0	0.118	8.00 (± 3.68)	1.70
2,4-D	0.950	0.173	3.51 (± 1.81)	—
Acetaminophen	0.390 (± 0.297)	6.70 (± 2.16)	9.70	34.5 (± 14.9)
Anthracene	14.9 (± 7.4)	1.07 (± 0.04)	7.83 (± 4.21)	—
Atrazine	4.77 (± 1.37)	3.51 (± 0.58)	3.22 (± 2.31)	—
Benzo(a)pyrene	16.4 (± 21.2)	1.08	25.2 (± 0.2)	—
Benzophenone	—	—	8.85 (± 0.21)	—
Bezafibrate	—	0.950	7.70 (± 0.42)	—
Bisphenol A	0.655 (± 0.276)	0.750	8.00 (± 3.11)	—
Bromoxynil	4.00	4.97	8.45 (± 0.40)	—
Caffeine	0.180 (± 0.030)	4.81	6.40 (± 0.71)	—
Carbamazepine	0.060 (± 0.009)	6.06 (± 0.03)	6.53 (± 3.36)	0.003 (± 0.002)
Carbofuran	1.66	0.800	1.73	—
Chlorpyrifos	1.60	0.650	4.54 (± 0.52)	—
Ciprofloxacin	1.19 (± 0.22)	17.2 (± 6.8)	5.94 (± 1.72)	—
Clofibric acid	27.5 (± 37.4)	0.927 (± 0.930)	4.95 (± 1.95)	0.376 (± 0.250)
DEET	—	1.21	4.95 (± 0.18)	—
Diazinon	4.95 (± 2.87)	2.95 (± 1.34)	8.70 (± 0.42)	—
Diclofenac	29.2 (± 8.6)	4.77 (± 1.16)	8.38 (± 1.25)	6.58 (± 4.00)
Diphenhydramine	12.5	0.388	6.26 (± 1.19)	—
Diuron	1.43 (± 0.41)	16.1 (± 0.4)	8.65 (± 5.73)	—
Doxycycline	0.803 (± 1.201)	48.4 (± 63.7)	4.62 (± 4.41)	—
E ₁	17.5 (± 24.7)	0.370 (± 0.036)	—	2.96

Table A-2. (Continued).

TOrcs	$\Phi_{\text{TOrc-254}}$ $\times 10^{-2}$ mol/Ein	$\epsilon_{\text{TOrc-254}}$ $\times 10^3$ M ⁻¹ cm ⁻¹	$k_{\text{TOrc}\cdot\text{OH}}$ $\times 10^9$ M ⁻¹ s ⁻¹	$\Phi_{\text{TOrc-sunlight}}$ $\times 10^{-2}$ mol/Ein
E ₂	5.50 (±1.70)	0.403 (±0.024)	9.70 (±6.22)	0.480
E ₃	—	0.234	—	0.480
EE ₂	5.59 (±1.95)	0.931 (±1.193)	10.3 (±0.7)	0.480
Fluoranthene	44.7	0.311	17.6	—
Gemfibrozil	—	3.45	10.0 (±0.6)	—
Ibuprofen	13.9 (±7.5)	0.269 (±0.018)	6.86 (±0.48)	0.023 (±0.028)
Indomethacin	—	14.9	—	0.043 (±0.006)
Iopromide	3.90 (±0.40)	21.0 (±0.2)	3.30 (±0.60)	—
Ketoprofen	29.8 (±8.7)	15.3 (±0.2)	6.89 (±2.14)	—
Linuron	1.86 (±2.47)	13.4 (±0.1)	4.30	—
MCPA	14.9	0.352	6.60	—
Mefenamic acid	0.470 (±0.140)	5.07 (±0.61)	11.0	0.008 (±0.007)
Metolachlor	45.6 (±21.8)	0.564 (±0.086)	6.96 (±2.00)	—
Metoprolol	3.47 (±4.12)	0.565 (±0.333)	7.51 (±0.80)	—
Naproxen	2.77 (±2.05)	4.00 (±0.70)	8.86 (±0.65)	3.10 (±0.71)
Nonylphenol	24.3 (±15.7)	0.400	11.0 (±2.0)	0.300
Norfloxacin	0.340 (±0.030)	16.0	1.00	4.30
Octylphenol	—	—	14.0 (±2.0)	—
Phenanthrene	0.690 (±0.050)	40.5	13.4	—
Phenol	2.55 (±0.64)	0.750 (±0.325)	8.57 (±4.77)	—
Progesterone	2.20 (±0.50)	17.0 (±0.4)	0.850	—
Propachlor	12.7 (±1.0)	0.421	4.45 (±0.21)	—
Pyrene	0.385	18.2	—	—
Ranitidine	—	—	15.0 (±2.0)	0.530
Roxithromycin	—	—	5.40 (±0.30)	0.020

Table A-2. (Continued).

TOrCs	$\Phi_{\text{TOrC-254}}$ $\times 10^{-2}$ mol/Ein	$\epsilon_{\text{TOrC-254}}$ $\times 10^3 \text{ M}^{-1}\text{cm}^{-1}$	$k_{\text{TOrC}\cdot\text{OH}}$ $\times 10^9 \text{ M}^{-1}\text{s}^{-1}$	$\Phi_{\text{TOrC-sunlight}}$ $\times 10^{-2}$ mol/Ein
Simazine	8.30	3.33	2.45 (± 0.50)	—
Sulfamerazine	—	—	7.80 (± 0.30)	—
Sulfamethoxazole	3.62 (± 0.86)	13.9 (± 4.3)	5.81 (± 1.72)	79.0 (± 41.0)
Testosterone	12.9 (± 13.6)	15.1 (± 0.8)	—	4.15 (± 0.77)
Tetracycline	0.380	8.82 (± 6.66)	7.70 (± 1.20)	—
Triclosan	34.0 (± 7.0)	1.80	5.45 (± 0.06)	4.00
Trimethoprim	0.118 (± 0.011)	3.51 (± 0.80)	7.09 (± 1.49)	—

Note: For parameters with more than one literature value, averages and standard deviations (in parentheses) are reported.

Table A-3. Properties used in AdDesignSTM for the 43 TOrCs in this study with available Freundlich isotherm constants, reported at ambient or near-ambient conditions. An expanded version of this table with corresponding sources is presented in Table A1-3.

TOrCs	Molar Volume m ³ /kmol	Boiling Point °C	Solubility mg/L	Vapor Pressure Pa	Freundlich Parameters K (mg/g)(L/mg) ^{1/n} 1/n	
1,4-DCB	0.133 ^a	174 ^b	8.13×10^1	2.32×10^{2d}	121	0.47
2,4-D	0.189 ^a	329	6.77×10^2	1.10×10^{-2d}	43.9	0.34
Acetaminophen	0.121	341	1.40×10^4	2.59×10^{-4}	153	0.35
Anthracene	0.196 ^a	340 ^b	4.00×10^{-2}	8.71×10^{-4d}	376	0.70
Atrazine	0.163	313	3.47×10^1	3.85×10^{-5d}	289	0.29
Benzo(a)pyrene	0.259 ^a	495 ^b	0.00×10^0	7.32×10^{-7d}	33.6	0.44
Bezafibrate	0.287	538	1.22×10^{0c}	8.16×10^{-9}	141	0.19
Bisphenol A	0.259 ^a	220 ^b	1.20×10^2	3.03×10^{-5}	20.7	0.18
Bromoxynil	0.124	329	1.30×10^2	6.29×10^{-6d}	201	0.18
Caffeine	0.133	431	2.16×10^4	9.77×10^{-7}	239	0.04
Carbamazepine	0.187	410.	1.12×10^2	1.17×10^{-5}	430.	0.38
Carbofuran	0.187	311	3.20×10^2	6.47×10^{-4d}	266	0.41
Chlorpyrifos	0.237	377	1.12×10^0	2.71×10^{-3d}	11.3	0.70
Ciprofloxacin	0.227	567	3.00×10^4	3.80×10^{-11}	32.2	0.45
Clofibric acid	0.170	321	5.83×10^{2c}	1.01×10^{-2}	71.0	0.25
Diazinon	0.261	366	4.00×10^1	1.20×10^{-2d}	3.63	0.33
Diclofenac	0.207	424	2.37×10^0	8.19×10^{-6}	304	0.08
Diphenhydramine	0.249	345	3.06×10^3	7.73×10^{-4}	95.7	0.80
Diuron	0.179	354	4.20×10^1	9.20×10^{-6d}	279	0.22
E ₁	0.232	392	3.00×10^1	6.79×10^{-1}	610.	0.41
E ₂	0.233	395	3.90×10^0	2.65×10^{-7}	2.65	0.33
E ₃	0.230	432	4.41×10^{2c}	1.25×10^{-9}	0.310	0.78
EE ₂	0.245	411	1.13×10^1	2.60×10^{-7}	2.15	0.28

Table A-3. (Continued).

TOrcs	Molar Volume m ³ /kmol	Boiling Point °C	Solubility mg/L	Vapor Pressure Pa	Freundlich Parameters K (mg/g)(L/mg) ^{1/n} 1/n	
Fluoranthene	0.162	384 ^b	2.60×10^{-1}	1.23×10^{-3d}	664	0.61
Ibuprofen	0.200	323	2.10×10^1	2.48×10^{-2}	122	0.17
Iopromide	0.364	885	2.38×10^{1c}	2.12×10^{-26}	71.7	0.30
Ketoprofen	0.212	404	5.10×10^1	1.95×10^{-4}	1.14	0.23
Linuron	0.185	366	7.50×10^1	1.91×10^{-4d}	159	0.23
MCPA	0.153	287 ^b	6.30×10^2	7.87×10^{-4d}	29.5	0.29
Mefenamic acid	0.201	398	2.00×10^1	7.77×10^{-6}	9.54	0.59
Metolachlor	0.258	282 ^b	5.30×10^2	4.19×10^{-3d}	233	0.13
Naproxen	0.192	380.	1.59×10^1	1.69×10^{-4}	12.1	0.37
Nonylphenol	0.236	295 ^b	6.35×10^0	3.15×10^{-3d}	250.	0.37
Norfloxacin	0.237	553	1.78×10^{5c}	1.11×10^{-9}	300.	0.17
Phenanthrene	0.196 ^a	340. ^b	1.15×10^0	1.61×10^{-2d}	215	0.44
Phenol	0.088	182 ^b	8.28×10^4	4.67×10^{1d}	21.0	0.54
Pyrene	0.210 ^a	404 ^b	1.40×10^{-1}	6.00×10^{-4d}	389	0.39
Ranitidine	0.265	415	2.47×10^{4c}	1.87×10^{-4}	404	0.21
Simazine	0.148	307	6.20×10^0	2.95×10^{-6d}	150.	0.23
Sulfamethoxazole	0.173	414	6.10×10^2	1.73×10^{-5}	227	0.22
Tetracycline	0.270	745	2.31×10^2	2.77×10^{-19}	105	0.56
Triclosan	0.194	374	1.00×10^1	6.20×10^{-4}	3.03	0.62
Trimethoprim	0.221	449	4.00×10^2	1.00×10^{-6}	142	0.18

^a Molar volume values were obtained from Software to Estimate Physical Properties in ETDOT10 package.

^b Boiling point values (1 atm) used experiment data provided by EPI SuiteTM.

^c Water solubility values were estimated by WSKOW v1.41 program in the EPI SuiteTM at room temperature.

^d Vapor pressure values used experimental data provided by EPI SuiteTM at room temperature.

Table A-4. Molecular structures for 20 TOrCs with at least five reported values of membrane rejections during RO treatment that were accompanied by NaCl rejection data.

TOrCs	Length nm	Thickness nm
Acetaminophen	0.933	0.186
Atrazine	1.21	0.228
Bisphenol A	1.23	0.220
Caffeine	0.819	0.186
Carbamazepine	1.03	0.207
DEET	1.09	0.187
Diclofenac	1.08	0.329
E ₁	1.18	0.316
E ₂	1.16	0.315
E ₃	1.21	0.377
EE ₂	1.26	0.605
Gemfibrozil	1.27	0.438
Ibuprofen	1.14	0.228
Ketoprofen	1.34	0.315
Mefenamic acid	1.08	0.186
Naproxen	1.27	0.332
Progesterone	1.27	0.376
Simazine	1.21	0.186
Sulfamethoxazole	1.40	0.290
Trimethoprim	1.31	0.218

Note: Geometric parameters were estimated using Materials Studio 4.0. Molecular length is the maximum distance between any two atoms in a single compound. Molecular thickness is the maximum distance between any two atoms on planes perpendicular to the direction of molecular length. An expanded version of this table for all 55 TOrCs, including molecular structures, is presented in Figures A1-1 to A1-10.

A.2.3 Biodegradability Predictions

BioWin is a user-friendly, fragment-based, quantitative structure-activity relationship (QSAR) program embedded in the EPI SuiteTM (v4.11) that can be used to assess biological wastewater treatment. The software requires the CAS # or details of compound structure.

There are seven BioWin versions, numbered 1-7. BioWin1 and BioWin2 estimate the probability of rapid biodegradation using multiple linear and nonlinear regression models, respectively, that were developed using a training set assembled by Syracuse Research Corporation (Howard et al. 1987; Howard et al. 1992; Boethling et al. 1994). BioWin3 and BioWin4 are based on a training set from 17 experts, who were surveyed to predict the times required for both ultimate (complete mineralization) and primary (initial step) biodegradation of chemicals on a semi-quantitative scale (Boethling et al. 1989, 1994). Developers employed 36 substructures and compound molecular weight as the 37 independent variables to estimate regression coefficients for the first four BioWin models (BioWin1 to BioWin4) (Boethling et al. 1994). BioWin5 and BioWin6 also employ multiple linear and nonlinear regression methods to estimate the chemical-specific probability of passing the ready biodegradation test from the Japanese Ministry of International Trade and Industry (MITI). The method uses 43 independent variables (42 substructures and compound molecular weight) as the basis of the regression equations (Tunkel et al. 2000). The first six BioWin models were developed to predict biodegradability under aerobic conditions. The most recently developed model, BioWin7, estimates the probability of compound degradation under anaerobic

(methanogenic) conditions (Meylan et al. 2007). Features of the seven BioWin models are summarized in Table A-5.

The first six versions of BioWin were compared in terms of predictive accuracy (Tunkel et al. 2000; Boethling et al. 2003; Posthumus et al. 2005) and reviewed from a user's perspective (Rücker et al. 2012). Model performances were measured against validation sets from a database consisting of biodegradation results from 305 pre-manufacture notices (i.e., chemicals not yet in commerce that are subject to testing requirements under the Toxic Substances Control Act.) BioWin3 to BioWin6 were generally more accurate than BioWin1 and BioWin2 in terms of biodegradability (Boethling et al. 2003). BioWin4 predictions correlated well with observed removals of PPCPs during aerobic biological secondary treatment (Blair et al. 2013). On that basis, the semi-quantitative output of BioWin4 (v4.10) was used to estimate TOrC biodegradability here.

Table A-5. Summary of input/output characteristics of BioWin Models.

Version	Description			
	O ₂ Condition	Output Data	Output Classification	Training Set
BioWin1	Aerobic	Probability of rapid biodegradation	≥ 0.5 Biodegrades fast < 0.5 Does NOT biodegrade fast	Database consisted of results from 4 types of test method-specific records for 186 chemicals evaluated as “biodegrades fast” and 109 chemicals as “does not biodegrade fast”
BioWin2	Aerobic	Probability of rapid biodegradation	≥ 0.5 Biodegrades fast < 0.5 Does NOT biodegrade fast	Database consisted of results from 4 types of test method-specific records for 186 chemicals evaluated as “biodegrades fast” and 109 chemicals as “does not biodegrade fast”
BioWin3	Aerobic	Ultimate biodegradation rates	5.0 hours; 4.0 days; 3.0 weeks; 2.0 months; 1.0 longer	Time required for ultimate (transformation to CO ₂ and H ₂ O) biodegradation of 200 chemicals on scales (hours = 5, days = 4, weeks = 3, months = 2, longer = 1) scored by 17 experts from survey study
BioWin4	Aerobic	Primary biodegradation rates	5.0 hours; 4.0 days; 3.0 weeks; 2.0 months; 1.0 longer	Time required for primary (initial metabolic step) biodegradation of 200 chemicals on scales (hours = 5, days = 4, weeks = 3, months = 2, longer = 1) scored by 17 experts from survey study
BioWin5	Aerobic	Probability of ready biodegradability	≥ 0.5 Readily degradable < 0.5 Not readily degradable	Database consisted of results from MITI test for 254 chemicals evaluated as “readily biodegradable” and 335 chemicals as “not readily biodegradable”
BioWin6	Aerobic	Probability of ready biodegradability	≥ 0.5 Readily degradable < 0.5 Not readily degradable	Database consisted of results from MITI test for 254 chemicals evaluated as “readily biodegradable” and 335 chemicals as “not readily biodegradable”
BioWin7	Anaerobic	Probability for methanogenic biodegradation	≥ 0.5 Biodegrades fast < 0.5 Does not Biodegrade fast	Results from serum bottle test for 82 chemicals evaluated as “pass” and 87 chemicals as “fail”

Table A-5. (Continued).

Version	Regression Method	Independent Variables	Model Algorithm	Classification Accuracy for Validation Set Chemicals ^a
BioWin1	Linear (least squares)	36 substructures + molecular weight	$Y_j = a_0 + \sum_{n=1}^{36} a_n f_n + a_m M_w + e_j = \begin{cases} 1, & \text{if biodegrades fast} \\ 0, & \text{if does not biodegrade fast} \end{cases}$	54% (165/305)
BioWin2	Non-linear (maximum likelihood)	36 substructures + molecular weight	$Y_j = \frac{\exp(a_0 + \sum_{n=1}^{36} a_n f_n + a_m M_w)}{1 + \exp(a_0 + \sum_{n=1}^{36} a_n f_n + a_m M_w)} = \begin{cases} 1, & \text{if biodegrades fast} \\ 0, & \text{if does not biodegrade fast} \end{cases}$	67% (203/305)
BioWin3	Linear (least squares)	36 substructures + molecular weight	$Y_j = a_0 + \sum_{n=1}^{36} a_n f_n + a_m M_w + e_j$	87% (265/305)
BioWin4	Linear (least squares)	36 substructures + molecular weight	$Y_j = a_0 + \sum_{n=1}^{36} a_n f_n + a_m M_w + e_j$	83% (253/305)
BioWin5	Linear (least squares)	42 substructures + molecular weight	$Y_j = a_0 + \sum_{n=1}^{42} a_n f_n + a_m M_w + e_j = \begin{cases} 1, & \text{if readily biodegradable} \\ 0, & \text{if not readily biodegradable} \end{cases}$	83% (252/305)
BioWin6	Non-linear (maximum likelihood)	42 substructures + molecular weight	$Y_j = \frac{\exp(a_0 + \sum_{n=1}^{42} a_n f_n + a_m M_w)}{1 + \exp(a_0 + \sum_{n=1}^{42} a_n f_n + a_m M_w)} = \begin{cases} 1, & \text{if readily biodegradable} \\ 0, & \text{if not readily biodegradable} \end{cases}$	83% (254/305)
BioWin7	Linear (least squares)	37 substructures	$Y_j = a_0 + \sum_{n=1}^{37} a_n f_n + e_j = \begin{cases} 1, & \text{if serum bottle test pass} \\ 0, & \text{if serum bottle test not pass} \end{cases}$	89.9% (152/169)

^a Validation set applied for classification accuracy test was described by Boethling et al. (2003) for the first six BioWin models (BioWin1 to BioWin6); and Meylan et al. (2007) for BioWin7.

A.2.4 UV₂₅₄ Photolysis

Photolytic processes employing monochromatic UV light (254 nm) are used in water treatment for disinfection or, in combination with hydrogen peroxide (H₂O₂), for advanced oxidation treatment. Some TOrCs are degraded by direct exposure to UV light (direct photolysis) or are destroyed by radicals and/or other active chemical species generated by UV irradiation of other compounds (indirect photolysis). Direct photolysis is envisioned as a two-step process in which the absorption of light energy promotes the compound to an excited state, after which either chemical transformation occurs or the excited compound devolves to its original ground state. Indirect photolysis is initiated through light absorption by other chemicals, leading to production of reactive intermediates such as reactive oxygen species (ROS) or photo-excited dissolved organic matter (DOM) that reacts chemically with the target compound (Schwarzenbach et al. 2003).

Direct and indirect photolysis of TOrCs in either pure water or in a representative wastewater secondary effluent were simulated for a model system consisting of a plug flow reactor (PFR) (cylindrical with concentrically-centered UV lamp, 140 cm length, 14 cm barrel inner diameter and 4 cm lamp sleeve outside diameter – light path length 5 cm – with 20 L chamber volume) that was equipped with a low pressure UV lamp with total irradiance of $1.0 \times 10^{-5} \text{ EinL}^{-1}\text{s}^{-1}$. Flow rate was selected to yield 30 s of residence time. For UV/H₂O₂ simulations, the H₂O₂ reactor influent concentration was 5 ppm (0.15 mM). For the representative secondary effluent used in simulations, an equivalent background compound (EBC) was used to approximate effluent organic matter (EfOM). Per methods

outlined by Rosario-Ortiz et al. (2008), the initial concentration of EBC was set as $6.67 \times 10^{-4} \text{ M}_c$ (molarity of EBC based on moles of carbon) assuming that the dissolved organic carbon (DOC) of the effluent matrix is 8 ppm, with a molar absorptivity of $240 \text{ M}_c^{-1} \text{ cm}^{-1}$. Matrix absorbance was 0.16 cm^{-1} at 254 nm. The second-order kinetic rate constant for reaction of EBC with $\cdot\text{OH}$ was assumed to be $k_{\text{EBC}\cdot\text{OH}} = 8.6 \times 10^8 \text{ M}_c^{-1} \text{ s}^{-1}$.

The rate of decomposition of a TOrC via direct photolysis under UV-254 light in the absence of other reactions in a well-mixed batch reactor is given by

$$\frac{d[\text{TOrC}]}{dt} = -\Phi_{\text{TOrC-254}} I_0 f (1 - 10^{-\text{Abs}_{254}}) \quad \text{Eq (A-2)}$$

where t is time,

$$f = \frac{\epsilon_{\text{TOrC-254}} [\text{TOrC}]}{\epsilon_{\text{TOrC-254}} [\text{TOrC}] + \epsilon_{\text{EBC-254}} [\text{EBC}]_c} \quad \text{Eq (A-3)}$$

is the fraction of light absorbed by the TOrC, and the total solution absorbance is

$$\text{Abs}_{254} = (\epsilon_{\text{TOrC-254}} [\text{TOrC}] + \epsilon_{\text{EBC-254}} [\text{EBC}]_c) \ell \quad \text{Eq (A-4)}$$

where $\Phi_{\text{TOrC-254}}$ is the TOrC quantum yield (mol/Ein) at 254 nm, I_0 is the incident light intensity from the reactor lamp ($\text{Ein L}^{-1} \text{ s}^{-1}$), $\epsilon_{\text{TOrC-254}}$ and $\epsilon_{\text{EBC-254}}$ are the molar absorptivities ($\text{M}^{-1} \text{ cm}^{-1}$ and $\text{M}_c^{-1} \text{ cm}^{-1}$) of the target and EBC at 254 nm, respectively, and ℓ is the UV path length (cm). In pure water, $[\text{EBC}] = 0 \text{ M}_c$. Quantum yields and extinction coefficients for the TOrCs studied here are presented in Table A1-1.

Eq (A-2) is also applicable to a plug-flow reactor, with time being equivalent to residence time at points along the reactor.

When H_2O_2 is present, the attenuation of TOrCs involves both direct and indirect photolysis. In this case, indirect photolysis was assumed to be due to the production of $\cdot\text{OH}$ from H_2O_2 photolysis only. Under these conditions, the rate of disappearance of the TOrC is given by

$$\frac{d[\text{TOrC}]}{dt} = -\Phi_{\text{TOrC}-254} I_0 f (1 - 10^{-\text{Abs}_{254}}) - k_{\text{TOrC}-\cdot\text{OH}} [\cdot\text{OH}] [\text{TOrC}] \quad \text{Eq (A-5)}$$

where

$$f = \frac{\epsilon_{\text{TOrC}-254} [\text{TOrC}]}{\epsilon_{\text{TOrC}-254} [\text{TOrC}] + \epsilon_{\text{H}_2\text{O}_2-254} [\text{H}_2\text{O}_2] + \epsilon_{\text{EBC}-254} [\text{EBC}]_c} \quad \text{Eq (A-6)}$$

and

$$\text{Abs}_{254} = (\epsilon_{\text{TOrC}-254} [\text{TOrC}] + \epsilon_{\text{H}_2\text{O}_2-254} [\text{H}_2\text{O}_2] + \epsilon_{\text{EBC}-254} [\text{EBC}]_c) \ell \quad \text{Eq (A-7)}$$

In Eq (A-5), $k_{\text{TOrC}-\cdot\text{OH}}$ is the second-order reaction rate constant ($\text{M}^{-1}\text{s}^{-1}$) for the reaction of $\cdot\text{OH}$ with the TOrC and $\epsilon_{\text{H}_2\text{O}_2-254}$ is the molar absorptivity ($\text{M}^{-1}\text{cm}^{-1}$) of H_2O_2 at 254 nm. A complete mechanism for the UV/ H_2O_2 -based advanced oxidation process (AOP) is provided (Table A-6). In reaction simulations, initial concentrations of all TOrCs were arbitrarily set at 10 nM, equivalent to the low ppb range, since molecular weights of the selected compounds are essentially all > 100 g/mol (phenol, 94.11 g/mol being the lone exception). Concentrations of most TOrCs in treated effluent and surface waters range from non-detectable to a few ppb (Kolpin et al. 2002; Miège et al. 2009). A model based on Eq (A-5) and mole balances for all reactive species (Table A-6) was developed in MATLAB (R2012b). The system of ordinary differential equations (ODEs)/algebraic equations was solved using the MATLAB ode15s solver.

Table A-6. Summary of reactions and related parameters used to simulate UV₂₅₄-based treatment performance of TOrCs.

Reaction ID	Reaction	Kinetic Parameters	Reference
R1	$\text{H}_2\text{O}_2 + h\nu \rightarrow 2 \cdot\text{OH}$	$\epsilon_{\text{H}_2\text{O}_2-254} = 18.7 \text{ M}^{-1}\text{cm}^{-1}$ $\Phi_{\text{H}_2\text{O}_2-254} = 0.5 \text{ mol/Ein}$	Volman and Chen (1959)
R2	$\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{O}_2^{\cdot-} + \text{H}_2\text{O} + \text{H}^+$	$k_2 = 2.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R3	$\cdot\text{OH} + \text{HO}_2^- \rightarrow \text{O}_2^{\cdot-} + \text{H}_2\text{O}$	$k_3 = 7.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R4	$\cdot\text{OH} + \text{HO}_2\cdot \rightarrow \text{O}_2 + \text{H}_2\text{O}$	$k_6 = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R5	$\cdot\text{OH} + \text{O}_2^{\cdot-} \rightarrow \text{O}_2 + \text{OH}^-$	$k_7 = 8.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R6	$\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$	$k_8 = 5.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R7	$\text{O}_2^{\cdot-} + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{O}_2 + \text{OH}^-$	$k_{10} = 0.13 \text{ M}^{-1}\text{s}^{-1}$	Bielski et al. (1985)
R8	$\text{O}_2^{\cdot-} + \text{HO}_2\cdot \rightarrow \text{HO}_2^- + \text{O}_2$	$k_{12} = 9.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Bielski et al. (1985)
R9	$\text{HO}_2\cdot + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k_{13} = 8.6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	Weinstein and Bielski (1979)
R10	$\text{HO}_2\cdot + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{O}_2 + \text{H}_2\text{O}$	$k_{14} = 3.7 \text{ M}^{-1}\text{s}^{-1}$	Bielski et al. (1985)
R11	$\text{H}_2\text{O}_2 \leftrightarrow \text{HO}_2^- + \text{H}^+$	$k_{18} = 2.51 \times 10^{-2} \text{ s}^{-1}$ $k_{18r} = 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Perry et al. (1984)
R12	$\text{HO}_2\cdot \leftrightarrow \text{O}_2^{\cdot-} + \text{H}^+$	$k_{19} = 1.58 \times 10^5 \text{ s}^{-1}$ $k_{19r} = 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Perry et al. (1984)
R13	$\text{TOrC} + h\nu \rightarrow \text{products}$	$\epsilon_{\text{TOrC-254}}$ $\Phi_{\text{TOrC-254}}$	Table A-2
R14	$\text{TOrC} + \cdot\text{OH} \rightarrow \text{products}$	$k_{\text{TOrC}\cdot\text{OH}}$	Table A-2
R15	$\text{EBC} + \cdot\text{OH} \rightarrow \text{products}$	$k_{\text{EBC}\cdot\text{OH}} = 8.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Rosario-Ortiz et al. (2008)

Note: Average values of $\epsilon_{\text{TOrC-254}}$, $\Phi_{\text{TOrC-254}}$ and $k_{\text{TOrC}\cdot\text{OH}}$ from Table A-2 were used in modeling.

A.2.5 Activated Carbon Adsorption

The software AdDesignSTM from the Environmental Technologies Design Options Tool (ETDOT10) package developed by Michigan Technological University was used to predict TOrC removals by activated carbon treatment. AdDesignSTM provides three separate adsorption model scenarios: (i) equilibrium column model (ECM), (ii) constant pattern homogeneous surface diffusion model (CPHSDM), and (iii) pore and surface diffusion model (PSDM), to simulate gas- and liquid-phase adsorption in fixed bed adsorbers. The PSDM, a dynamic fixed bed model considering external and intraparticle mass transfer resistance, was used in this study to evaluate adsorption performance with and without fouling of activated carbon by organic matter. Convective mass transfer coefficients, and pore and surface diffusion coefficients of TOrCs required by the PSDM were estimated by AdDesignSTM. Adsorption simulations were performed for solutions involving single TOrCs at initial concentrations of 10 nM in either organic free water—i.e. without fouling, or Rhine river (Germany) water with anthropogenic input, as specified for “Fouling of GAC” options of the program. Adsorber characteristics and operating conditions were arbitrarily set at 2.0 m length, 3.66 m diameter, 8500 kg total mass of carbon, and 1.89 m³/min liquid flow rate, to represent a full-scale activated carbon process. In addition, the empty bed contact time (EBCT) was set to 11 minutes; 0.40 g/mL was the bed density, and 25 °C was the water temperature at 1 atm pressure. Spherical particles of Calgon F400 (12 × 40) activated carbon were selected as adsorbent. Adsorption isotherm parameters for the TOrCs studied here are presented in Table A1-3. Results of the simulation include bed volumes fed to breakthrough (BVF), volume treated per mass of adsorbent (VTM, m³/kg), length of the mass transfer zone (MTZ, cm) and

breakthrough time. BVF was chosen to represent the chemical-specific propensity for adsorptive removal. Breakthrough was defined as the point where the exit concentration reached 5% of the inlet concentration.

A.2.6 Membrane Separations

Published data were used to examine the compound-specific separation efficiencies achievable through RO and NF. TOrC rejection data reported without corresponding sodium chloride (NaCl) rejections were excluded. Simultaneous TOrC and NaCl rejections were obtained from the literature for 20 compounds (≥ 5 data points were required for inclusion in the dataset). Linear regression of data representing TOrC rejection versus NaCl rejection was carried out using Microsoft Excel 2010. Detailed information is provided in the supplementary information (Figures A1-11 to A1-15 and Table A1-4). TOrC rejection at 50% NaCl rejection was then determined from regression lines specific to each TOrC, and values were compared to key physicochemical properties, including molecule length and thickness and $\log D_{ow}$, to explore mechanism-based explanations for membrane removal efficiencies.

A.2.7 Sunlight Photolysis

Treated wastewater is often discharged to waters exposed to sunlight, where direct and indirect photolysis may contribute to compound disappearance (Fono et al. 2006; Jasper and Sedlak 2013). In those situations, both natural organic matter (NOM) and effluent organic matter (EfOM) may act as photo-sensitizers for indirect photolytic reactions (Lee et al. 2013, Zhang et al. 2014, Dong et al. 2015). In addition, both NOM and EfOM contribute to light absorption, which reduces the light available for TOrC and H_2O_2

absorption (shading effect). TOrC transformations during solar irradiation with and without matrix shading were simulated in the following conditions: an open-top well-mixed cylindrical batch reactor (2 m² top surface area and 1 m³ volume) with 0.5-m light path length containing individual TOrCs in either pure water or secondary effluent from the Tres Rios Wastewater Reclamation Facility (TRWRF) in Tucson, AZ. Samples were exposed to sunlight over an eight-hour period from 8 am to 4 pm.

Instantaneous rates of TOrC transformation by direct photolysis in sunlight at UVA wavelengths are given by (Rojas et al. 2011)

$$\frac{d[\text{TOrC}]}{dt} = -C(t)\Phi_{\text{TOrC-sunlight}} \int_{300}^{400} I_{\lambda} f_{\lambda} (1 - 10^{-\text{Abs}_{\lambda}}) d\lambda \quad \text{Eq (A-8)}$$

where

$$f_{\lambda} = \frac{\epsilon_{\text{TOrC-}\lambda} [\text{TOrC}] \ell}{\epsilon_{\text{TOrC-}\lambda} [\text{TOrC}] \ell + \text{Abs}_{\text{matrix-}\lambda}} \quad \text{Eq (A-9)}$$

and

$$\text{Abs}_{\lambda} = \epsilon_{\text{TOrC-}\lambda} [\text{TOrC}] \ell + \text{Abs}_{\text{matrix-}\lambda} \quad \text{Eq (A-10)}$$

In addition, $\Phi_{\text{TOrC-sunlight}}$ is the average sunlight quantum yield (mol/Ein) for the TOrC modeled in the wavelength range 300 to 400 nm, I_{λ} is the noon-time ground level global spectral irradiance (EinL⁻¹s⁻¹nm⁻¹) at wavelength λ , $\epsilon_{\text{TOrC-}\lambda}$ is the spectral molar absorptivity (M⁻¹cm⁻¹) of the TOrC at wavelength λ , $\text{Abs}_{\text{matrix-}\lambda}$ is the water matrix absorbance at λ based on a 0.5-m light path, Abs_{λ} is the total solution absorbance at λ , and ℓ is the light path length (cm). The function $C(t)$ represents the light intensity at time t as a fraction of the light intensity at noon. The ground level global spectral irradiance in

Tucson, AZ, on June 12, 2015 (from 8 am to 4 pm, local time) was obtained from the Simple Model of the Atmospheric Radiative Transfer of Sunshine (SMARTS, 2.9.5 PC package from National Renewable Energy Laboratory) and used in all computations. The function $C(t)$ is a second-order polynomial obtained by fitting the SMARTS-calculated spectral irradiance. Details of the calculation method were provided by Rojas et al. (2011). In pure water, $Abs_{matrix-\lambda}$ is zero throughout the wavelength interval 300 - 400 nm while $Abs_{matrix-\lambda}$ is obtained from a secondary effluent sample collected from the TRWRF. Detailed information about sunlight spectral irradiance, $\epsilon_{TOrc-\lambda}$, $Abs_{matrix-\lambda}$ as well as the effluent quality is given in the supplemental materials (Figure A1-16 and Table A1-5). Attenuation was predicted for each TOrc individually using an initial TOrc concentration of 10 nM and fluid matrices consisting of either pure water or wastewater effluent. Model outputs are the fractional removals of individual TOrcs by direct photolysis. Quantum yields for the TOrcs studies are presented in Table A1-2.

A.2.8 Statistical Analysis

The Spearman's rank correlation method (Myers and Well 2003) was employed for analysis of potential relationships between process efficiencies and compound-specific physicochemical properties. The Spearman coefficient ρ (ranging from -1 to +1) is a monotonic, non-linear measure of strength of relationship between rank orders of two variables. Values of +1 and -1 indicate perfect correspondence (direct and inverse) between the ordered values of those variables. Value near 0 suggests that there is no relationship.

A.3 Results and Discussion

The results represent efforts to anticipate individual TOrC removals during unit processes that are specific to conventional and advanced municipal wastewater treatment. Advanced treatment processes include those that are commonly relied upon to protect human health when potable reuse of treated wastewater is contemplated—i.e., direct photolysis, UV/H₂O₂ advanced oxidation, carbon adsorption and RO or NF. Photolysis of TOrCs in sunlight is also considered as a means to further purify treated water following discharge to natural waters. In most of these areas, simulations are supported by empirical data necessary for model calibration/verification. In a few instances, where models appear to be insufficiently reliable, an entirely empirical approach to compound removal or transformation is taken.

A.3.1 BioWin Biodegradability Predictions

Biodegradability was predicted by BioWin (versions 1 to 7) using the procedures specified above. Results are summarized in Table A1-6 of the supplementary information. Per the Methods section, we selected results obtained with BioWin4 as biodegradability predictors for further use. Those results consist of estimated (compound-dependent) times required for primary metabolic transformations on a semi-quantitative scale. Predicted transformation times were ranked and divided into five groups ranging in duration from days to months for the 55 selected TOrCs (Figure A-1). The wide range of biodegradability indices of the 55 TOrCs considered reflects the diversity present among their molecular structures. In particular, PAHs were less biodegradable than other groups.

Predicted hormone biodegradabilities were generally lower than those of pesticides, herbicides and pharmaceuticals.

Figure A-1. Predicted semi-quantitative biodegradation indices (BioWin4) for 55 TORCs. TORC IDs in this and following figures are summarized in Table A-1. The number designations for specific TORCs in Figure A-1 are preserved throughout APPENDIX A.

The pH-7 octanol-water partition coefficient (D_{ow}), which is frequently used to represent conditional hydrophobicity (at circumneutral pH) was examined here as a potential contributor to TOrC biodegradability. BioWin4 results are presented as a function of $\log D_{ow}$ values in Figure A-2. Results of the statistical analysis suggest that compound hydrophobicity does not contribute to (BioWin4) biodegradability. Nevertheless, influent-to-effluent reduction in compound concentration occurs in part as a consequence of biosorption and sludge separation, so that BioWin predictions may not be an adequate indication of overall process performance. That is, removal of less biodegradable, hydrophobic TOrCs during conventional secondary treatment may be due primarily to adsorption on biosolids. TOrCs such as EE₂ (26) and triclosan (54), for example, which have low BioWin4 indices but high D_{ow} values, are, in general, efficiently removed during conventional biological treatment. Although sorption of TOrCs is usually considered a minor contributor to removal during biological treatment (Radjenović et al. 2009; Khan and Ongerth 2004), sorption to sludge solids increases dramatically for compounds with $\log K_{ow} > 4$ (Byrns 2001; Khan and Ongerth 2004; Thompson et al. 2011).

Figure A-2. Calculated BioWin4 biodegradation indices as a function of $\log D_{ow}$. Compound IDs correspond to those in Figure A-1. The Spearman correlation coefficient (ρ) is shown.

To minimize the effects of biosorption among reported data, TOrCs with $\log D_{ow} \geq 3.5$ were eliminated from further consideration. For the remaining TOrCs, levels of compound removal that exceeded 80% of influent-to-effluent measurements during activated sludge treatment, as reported by Rojas et al. (2013), were plotted as a function of the compound-specific BioWin4 index (Figure A-3). The objective was to better examine the relationship between observed efficiencies of biochemical transformation and BioWin4 predictions of biodegradability—i.e., to exclude compounds with a strong tendency to adsorb on biosolids. Even though the Spearman correlation coefficient increased, the relationship between the BioWin4 index and observed removals during activated sludge treatment was weak ($\rho = 0.27$). This is contradictory to the results of

Blair et al. (2013), who found that BioWin4 indices were well correlated with observed removals of PPCPs. It is possible that the wide variety of operating conditions during conventional wastewater treatment is partly responsible for the apparent lack of correlation, although the inherent complexity of biodegradation processes probably would make finding successful correlations difficult.

Figure A-3. Relationship between levels of removal of TOrCs observed with > 80% frequency (from Rojas et al. 2013) as a function of the BioWin4 (bioremediation) index. Only TOrCs with $\log D_{ow} < 3.5$ were considered to minimize the effect of sorptive removal. The Spearman correlation coefficient (ρ) is shown. Data correspond to measurements from full-scale wastewater treatment plants.

A.3.2 UV_{254} Direct Photolysis

Direct UV photo-attenuations were calculated under the conditions presented in the Methods section for all 45 TOrCs for which both quantum yield and molar absorptivity literature data at 254 nm were found. Results are shown for both clean matrix and

wastewater effluent simulations (Figure A-4). Six out of 45 of the TOrCs studied were transformed at more than 50% level during low-pressure UV irradiation in treated wastewater under the conditions of the simulations. Fourteen were transformed at more than 50% level under the same conditions in the pure water matrix. The differences shown in Figure A-4 between clean water and secondary effluent clearly indicate the relatively high impact that light shading has on photolytic transformations, since light shading was the only effect included in the matrix effects during the modeling of the process.

Figure A-4. Predicted influent-to-effluent removal of 45 TOrCs in pure water and secondary effluent by direct photolysis during UV-254 treatment. Conditions for the simulation were as indicated in the Methods section. In all cases, $[TOrCs]_0 = 10 \text{ nM}$.

Once reactor characteristics and operating conditions are set, including EBC parameters, Eq (A-2) shows that direct-photolysis removal efficiencies depend on just two

parameters: ϵ_{254} and Φ_{254} . The influence of these parameters is shown in Figure A-5. The straight-line shape of the removal contours in the log-log scale is a consequence of the low concentrations on TOrCs used in the simulations. Since the initial concentration of TOrCs is in all cases 10 nM, compounds with sufficiently low molar absorptivity will satisfy $\text{Abs}_{254} \ll 1$. For that case, neglecting the higher order terms in a Taylor series expansion of the exponential term in Eq (A-2) yields

$$\frac{d[\text{TOrC}]}{dt} \approx -2.303\Phi_{\text{TOrC}-254}I_o(\epsilon_{\text{TOrC}-254}[\text{TOrC}]\ell) \quad \text{Eq (A-11)}$$

which, after integration, leads to

$$\ln \frac{[\text{TOrC}]}{[\text{TOrC}]_o} = -2.303\Phi_{\text{TOrC}-254}\epsilon_{\text{TOrC}-254}I_o\ell t \quad \text{Eq (A-12)}$$

Note that under these conditions, TOrC removal depends on the product between quantum yield and extinction coefficient, so that this combination of the two parameters represents a single independent variable.

In the wastewater matrix, if the solution absorbance at 254 nm is overwhelmed by EBC—i.e. $\epsilon_{\text{TOrC}-254}[\text{TOrC}] \ll \epsilon_{\text{EBC}-254}[\text{EBC}]$, Eq (A-2) can be simplified to

$$\frac{d[\text{TOrC}]}{dt} \approx -\Phi_{\text{TOrC}-254}\epsilon_{\text{TOrC}-254}[\text{TOrC}]I_o \frac{[1 - 10^{-(\epsilon_{\text{EBC}-254}[\text{EBC}]_c)\ell}]}{\epsilon_{\text{EBC}-254}[\text{EBC}]_c} \quad \text{Eq (A-13)}$$

If EBC concentration is unchanged by UV irradiation, Eq (A-13) can be integrated yielding

$$\ln \frac{[\text{TOrC}]}{[\text{TOrC}]_o} = -\Phi_{\text{TOrC}-254}\epsilon_{\text{TOrC}-254}I_o \frac{[1 - 10^{-(\epsilon_{\text{EBC}-254}[\text{EBC}]_c)\ell}]}{\epsilon_{\text{EBC}-254}[\text{EBC}]_c} t \quad \text{Eq (A-14)}$$

Figure A-5. Predicted UV-254 direct photolysis removals of TOrCs at 10 nM initial concentration in secondary effluent as a function of compound-specific molar absorptivity and quantum yield at 254 nm. Simulation results for specific TOrCs are as shown. Compound identities are indicated by number as described in Figure A-1. Conditions for the simulations are described in the Methods section.

Consequently, the log transformed TOrC residuals are also proportional to the product of their molar absorptivity and quantum yield at 254 nm. To establish the validity of these approximations for the treatment process considered here, predicted residual fractions of 45 TOrCs in pure water and effluent, calculated from Eq (A-2), were plotted as a function of the TOrC-dependent product of ϵ_{254} and Φ_{254} and compared to results of Eq (A-12) and Eq (A-14) (Figure A-6). In both pure water and effluent, the straight-line shape of the relation presented establishes the validity of each approximation throughout the range of experimental conditions simulated and for each of the compounds tested. Matrix effects

are exceptionally important, as indicated by differences between the clean water and effluent lines.

Figure A-6. Residual (fractional) concentrations of 45 TOrcs from simulations of direct UV-254 photolysis under representative conditions in clean water and treated wastewater. The solid and dashed lines were generated using Eq (A-12) and Eq (A-14), respectively.

A.3.3 Advanced Oxidation

Transformations of TOrcs by UV/H₂O₂ AOP treatment were simulated using the plug-flow reactor configuration and operating conditions specified in the Methods section. The concentration of H₂O₂ added to both the clean water and effluent matrices was 5 ppm. A third set of calculations was performed in which the shading effect of the wastewater matrix was neglected by artificially imposing $\epsilon_{\text{EBC-254}} = 0$. That calculation represents a hypothetical situation designed to expose the effect of $\cdot\text{OH}$ scavenging by matrix organics. Results of the simulations are presented in Figure A-7. Under the conditions

selected for the simulations, AOP removal efficiency in pure water was high ($> 80\%$, but mostly close to 100%) for all TOrCs. Although photosensitivities—i.e. the product of ϵ_{254} and Φ_{254} , among the 42 selected TOrCs ranged from $< 2 \text{ LEin}^{-1}\text{cm}^{-1}$ (2,4-D, ID #2) to over $4500 \text{ LEin}^{-1}\text{cm}^{-1}$ (ketoprofen, ID #32), the range of second-order reaction rate constants for the same compounds with $\cdot\text{OH}$ is roughly 10^9 to $10^{10} \text{ M}^{-1}\text{s}^{-1}$, close to the diffusion limit, accounting for the predicted AOP efficiency in the clean matrix.

Figure A-7. Predicted fractional TOrC attenuations during UV/H₂O₂ for 42 TOrCs with reported $\Phi_{\text{TOrC-254}}$, $\epsilon_{\text{TOrC-254}}$ and $k_{\text{TOrC}\cdot\text{OH}}$ values in three different matrices: PW = pure water, SE = secondary effluent, HSE effluent w/o shading = hypothetical secondary effluent neglecting light shading effect. Operating conditions are representative of practice: commercial size PFR with low pressure UV, 30 s residence time, $[\text{TOrCs}]_0 = 10 \text{ nM}$, $[\text{H}_2\text{O}_2]_0 = 5 \text{ ppm}$ (Methods section).

In the effluent matrix (secondary effluent), however, both shading and scavenging of $\cdot\text{OH}$ by matrix organics are predicted to inhibit TOrC removal efficiencies. Consequently,

TOrC removal efficiencies were only marginally improved by the addition of H_2O_2 to the wastewater matrix. This can be seen by comparison of results in Figures A-4 and A-7 (black bars for direct photolysis in Figure A-4 versus cyan bars in Figure A-7, which accounted for shading and radical scavenging effects.)

As mentioned, the pure water efficiencies are uniformly high (gray bars in Figure A-7). Effects of radical quenching by reaction with wastewater constituents are as shown (yellow vs. gray bars), as are the combined effects of wastewater quenching and shading (reaction plus UV absorbance; cyan bars).

A.3.4 Carbon Adsorption

A correlation between $\log K_{ow}$ and adsorption performance is usually acknowledged in the literature (Hu et al. 1997; Westerhoff et al. 2005). The same idea was pursued by plotting AdDesignSTM (PSDM) predicted bed volumes fed to breakthrough (BVF) in organic free water—i.e. without fouling adsorbent by NOM, as a function of $\log D_{ow}$ for the 35 TOrCs with available $\log D_{ow}$ values (Figure A-8). The results indicate that $\log D_{ow}$ is a poor indicator of the predicted performance of carbon adsorption. The lack of correlation may be due at least in part to the lack of a consistent isotherm parameter database. The Freundlich parameters assembled in this study represent values taken over 15 different types of activated carbon at pH values ranging from 2.0 to 8.0. Nevertheless, correlation between $\log D_{ow}$ and adsorption performance was not substantially improved by applying Freundlich parameters from a single source (detailed information available in Table A1-7 and Figure A1-17).

Figure A-8. AdDesignSTM (PSDM) predicted BVF to breakthrough for TOxCs in organic free water versus compound-specific $\log D_{ow}$ values (Table A-1). The Spearman correlation coefficient (ρ) for the hypothesized relationship is shown.

The BVF to breakthrough for 43 TOxCs with available Freundlich parameters and related physicochemical information were calculated for the conditions specified in the Methods section to investigate potential impact of fouling on treatment efficiency. The results are shown in Figure A-9. The water matrices used were either NOM-free water or Rhine River (Germany) water, which contains a significant anthropogenic input. Those waters were among the selections available in AdDesignSTM under “Fouling of GAC”.

Figure A-9. Calculated BVF to breakthrough using AdDesignSTM (PSDM) for 43 TOrcs in either organic free water—i.e. without fouling, or Rhine River (Germany) water with anthropogenic input. Both are options within “Fouling of GAC” of the PSDM. In all cases, $[TOrcs]_0 = 10 \text{ nM}$.

In the presence of fouling by NOM, calculated BVFs ranged from approximately 10^2 to 10^6 . Values for diclofenac (19) and caffeine (11) were $> 5 \times 10^6$. Conversely, E_3 (25) was predicted to break through first at ~ 200 bed volumes. All other TOrcs were scattered between 10^3 and 10^6 . As expected, fouling of the activated carbon by NOM in the matrix inhibits TOrc separation, which is particularly noted for pesticides and herbicides. The pore and surface diffusion model (PSDM) from AdDesignSTM reduces the Freundlich capacity parameter (K) to reflect the fouling process. Fouling effects are specific to water quality characteristics, sorbate types and adsorbent properties (Bhuvendralingam 1992). When the fluid matrix and adsorber conditions are fixed, TOrc Freundlich capacity

parameters are corrected by the PSDM using empirical equations that are sorbate and sorbent specific.

A.3.5 Membrane Separations

Membrane TOrC rejection at 50% NaCl rejection was determined from linear regression lines specific to each TOrC. Examples of the regression are shown in Figure A-10. Only membrane separation literature data that were accompanied by NaCl rejection data were used in the analysis that follows. In addition, TOrCs lacking the five independent data points deemed sufficient for determination of the compound-specific rejection at 50% NaCl rejection were also neglected. Twenty TOrCs survived these screening criteria. Compound-specific rejections at the 50% NaCl rejection conditions are presented in Figure A-11.

Figure A-10. Relationship between TOrC and NaCl rejections for specific TOrCs. Examples include TOrCs with molecule thickness < 0.25 nm: atrazine and bisphenol A; and thickness > 0.3 nm: EE₂ and ketoprofen. Compound thicknesses, as defined in the text, are in parentheses. Solid lines are linear fit of the data. Similar analyses for other compounds are provided in Figures A1-11 to A1-15.

Figure A-11. NF/RO rejections of individual TORCs under conditions that resulted in 50% rejection of NaCl. Compounds analyzed in this fashion were limited to the 20 TORCs for which sufficient experimental data were available (Methods section).

To determine whether rejection data were influenced by TORC molecular dimensions or hydrophobicity, compound-specific rejections (Figure A-11) were examined as a function of $\log D_{ow}$, molecule length and thickness for each compound. Only TORC thickness proved to be a reasonable predictor of compound removal. The relationship is shown in Figure A-12. Figures illustrating potential relationships between membrane separation efficiency and either compound molecular length or hydrophobicity are omitted for brevity. (For details see Figure A1-18.)

A reciprocal function

$$y = 102.2 - \frac{4.481}{(x - 0.1)} \quad \text{Eq (A-15)}$$

wastewater effluent (Lee et al. 2013; Jasper and Sedlak 2013; Dong et al. 2015). Despite their potential importance, the current state of the art does not support rational quantification of indirect photolysis matrix effects due to EfOM; consequently, they are omitted from the following analysis. Furthermore, parameters governing direct photochemical transformations of TOrCs in sunlight (i.e. ϵ_{λ} and quantum efficiencies from 300 to 400 nm) are limited. Only 17 out of the 55 selected TOrCs could be analyzed here based on literature data. Results are presented in Figure A-13. As in direct UV photolysis, the shading effect of the effluent matrix is predicted to reduce photolytic efficiency in direct sunlight significantly. Important exceptions included acetaminophen (3), norfloxacin (40) and sulfamethoxazole (51), each of which is exceptionally sensitive to sunlight.

Figure A-13. Predicted removals of 17 TORCs in pure water and wastewater effluent due to direct photolysis in sunlight. The assumed period of exposure is 8 hours. Other conditions in the simulations were as indicated in the Methods section.

TORC removals in sunlight versus UV irradiance were sometimes inconsistent. That is, a subset of the TORCs analyzed was significantly more sensitive to sunlight than UV exposure (e.g., acetaminophen). The reverse was true for an additional set of the compounds analyzed (e.g., testosterone). Detailed information is provided in supplemental materials (Figure A1-19).

A.4 Implication for Process Design

Based on the foregoing, it is possible to comment on the efficacy of individual unit operations including conventional wastewater biotreatment, candidate tertiary processes and sunlight photolysis on the fates of the most prevalent TOrCs during and immediately after treatment of municipal wastes. Compound-specific TOrC treatment performance in effluent wastewater matrix of engineered and natural processes investigated in this study are shown in Table A-7.

Table A-7. Summary of treatment efficiency of different processes investigated in this study on attenuating TOrCs.

TOrCs	Conventional activated sludge process ^a	UV254 photolysis	UV/H ₂ O ₂ AOP	Activated carbon	RO/NF	Direct sunlight photolysis
	Levels of influent-to- effluent removal of TOrCs observed with > 80% frequency (%)	Predicted liquid removal (%)	Predicted liquid removal (%)	Bed volumes to breakthrough	Rejection (%) at 50% rejection of NaCl	Predicted liquid removal (%)
1,4-DCB	—	11	16	1.56×10^5	42 ^b	—
2,4-D	—	0	3	2.76×10^4	51 ^b	—
Acetaminophen	86	4	11	2.04×10^5	0	100
Anthracene	—	22	26	1.12×10^5	38 ^b	—
Atrazine	—	23	25	1.16×10^5	55	—
Benzo(a)pyrene	—	24	37	7.14×10^4	38 ^b	—
Benzophenone	67	—	—	—	0 ^b	—
Bezafibrate	49	—	—	2.69×10^5	84 ^b	—
Bisphenol A	69	1	6	1.01×10^5	36	—
Bromoxynil	—	27	31	1.37×10^5	0 ^b	—
Caffeine	84	1	6	7.10×10^5	70	—
Carbamazepine	3	1	5	3.72×10^5	77	0
Carbofuran	—	2	3	6.30×10^4	86 ^b	—
Chlorpyrifos	—	2	5	7.14×10^3	80 ^b	—
Ciprofloxacin	11	27	31	4.20×10^4	81 ^b	—
Clofibric acid	5	33	35	2.18×10^5	86 ^b	—
DEET	—	—	—	—	71	—

Table A-7. (Continued).

TOrCs	Conventional activated sludge process	UV254 photolysis	UV/H ₂ O ₂ AOP	Activated carbon	RO/NF	Direct sunlight photolysis
	Levels of influent-to- effluent removal of TOrCs observed with > 80% frequency (%)	Predicted liquid removal (%)	Predicted liquid removal (%)	Bed volumes to breakthrough	Rejection (%) at 50% rejection of NaCl	Predicted liquid removal (%)
Diazinon	—	21	25	2.35×10^3	82 ^b	—
Diclofenac	5	89	89	6.07×10^5	91	26
Diphenhydramine	—	7	12	1.74×10^4	86 ^b	—
Diuron	—	30	35	6.36×10^4	50 ^b	—
Doxycycline	—	46	47	—	89 ^b	—
E ₁	45	10	—	3.82×10^5	81	5
E ₂	45	3	10	2.42×10^4	91	22
E ₃	78	—	—	1.95×10^2	71	—
EE ₂	45	8	15	2.51×10^4	92	12
Fluoranthene	—	20	29	2.19×10^5	38 ^b	—
Gemfibrozil	36	—	—	—	81	—
Ibuprofen	70	6	10	2.67×10^5	68	1
Indomethacin	11	—	—	—	83 ^b	21
Iopromide	—	73	73	7.37×10^4	88 ^b	—
Ketoprofen	30	100	100	1.35×10^4	94	—
Linuron	—	32	34	9.31×10^4	50 ^b	—
MCPA	—	8	12	2.85×10^4	50 ^b	—
Mefenamic acid	—	4	11	1.31×10^4	67	3

Table A-7. (Continued).

TOrCs	Conventional activated sludge process	UV254 photolysis	UV/H ₂ O ₂ AOP	Activated carbon	RO/NF	Direct sunlight photolysis
	Levels of influent-to- effluent removal of TOrCs observed with > 80% frequency (%)	Predicted liquid removal (%)	Predicted liquid removal (%)	Bed volumes to breakthrough	Rejection (%) at 50% rejection of NaCl	Predicted liquid removal (%)
Metolachlor	—	33	36	1.44×10^5	86 ^b	—
Metoprolol	—	3	8	—	64 ^b	—
Naproxen	55	16	21	4.86×10^4	97	39
Nonylphenol	45	14	21	1.78×10^5	50 ^b	0
Norfloxacin	31	8	9	4.22×10^5	67 ^b	100
Octylphenol	53	—	—	—	50 ^b	—
Phenanthrene	—	36	41	2.25×10^5	38 ^b	—
Phenol	—	3	9	5.09×10^4	38 ^b	—
Progesterone	—	45	45	—	95	—
Propachlor	—	8	11	—	67 ^b	—
Pyrene	—	10	—	3.57×10^5	38 ^b	—
Ranitidine	22	—	—	3.76×10^5	50 ^b	86
Roxithromycin	21	—	—	—	93 ^b	36
Simazine	—	35	36	1.06×10^5	43	—
Sulfamerazine	—	—	—	—	79 ^b	—
Sulfamethoxazole	26	55	56	2.82×10^5	57	100
Testosterone	72	95	—	—	86 ^b	9
Tetracycline	52	5	10	7.12×10^4	94 ^b	—

Table A-7. (Continued).

TOrCs	Conventional activated sludge process	UV254 photolysis	UV/H ₂ O ₂ AOP	Activated carbon	RO/NF	Direct sunlight photolysis
	Levels of influent-to- effluent removal of TOrCs observed with > 80% frequency (%)	Predicted liquid removal (%)	Predicted liquid removal (%)	Bed volumes to breakthrough	Rejection (%) at 50% rejection of NaCl	Predicted liquid removal (%)
Triclosan	50	62	63	4.14×10^3	20 ^b	4
Trimethoprim	18	1	6	2.35×10^5	81	—

^a Data from Rojas et al. 2013.^b Evaluation based on calculated compound rejection.

Somewhat arbitrarily, process- and compound-specific TOrC removal efficiencies were characterized as high, medium or low according to the criteria presented in Table A-8. A scoring system was developed utilizing qualitative evaluation results based on the results in Table A-9 to provide semi-quantitative estimation for TOrCs removal efficiencies in wastewater effluent matrix of two proposed treatment sequences: (i) conventional secondary treatment followed by UV/H₂O₂ AOP followed by activated carbon followed by RO/NF, and (ii) conventional secondary treatment followed by UV/H₂O₂ AOP followed by activated carbon. In this scoring system, three qualitative attenuation levels—i.e. high, medium and low, of a single TOrC during each engineered processes were arbitrarily set as 2, 1 and 0, respectively. Removal scores of a TOrC during each selected engineered processes are independently summed, yielding a final score of the TOrC for selected treatment sequence. Results of this evaluation are presented in Table A-9. For sequence (i), one can consider such treatment strategy is good, fair or poor for removing a TOrC when final scores are > 5, 3-5, or < 3, respectively. When applying sequence (ii), final scores for good, fair or poor removal are > 4, 2-4, or < 2, respectively.

Table A-8. Summary of treatment evaluation of different processes investigated.

Unit Operation	Index	Determinants of process efficiency level		
		High	Medium	Low
Conventional activated sludge process	Influent-to-effluent removal (%)	> 75	25–75	< 25
UV254 Photolysis	Predicted liquid removal (%)	> 75	25–75	< 25
UV/H ₂ O ₂ AOP	Predicted liquid removal (%)	> 75	25–75	< 25
Activated carbon	Bed volumes fed to breakthrough	> 10 ⁵	10 ⁴ –10 ⁵	< 10 ⁴
RO/NF	Compound rej. @ NaCl Rej. = 50%	> 75	25–75	< 25
Sunlight photolysis	Predicted liquid removal (%)	> 75	25–75	< 25

Note: For compounds without enough reported data, their rejection percentages at NaCl rejection = 50% were calculated using Eq (A-15) based on compound molecular thickness data, which is provided in Figures A1-1 to A1-10.

Table A-9. Scoring system of semi—quantitative estimation for TOrCs removal efficiencies of proposed treatment sequence (i): conventional secondary treatment → UV/H₂O₂ AOP → activated carbon, and (ii): conventional secondary treatment → UV/H₂O₂ AOP → activated carbon → RO/NF.

TOrCs	Final Score	
	Sequence (i)	Sequence (ii)
Acetaminophen	4	4
Bisphenol A	3	4
Caffeine	4	5
Carbamazepine	2	4
Ciprofloxacin	2	4
Clofibric acid	3	5
Diclofenac	4	6
E ₂	2	4
EE ₂	2	4
Ibuprofen	3	4
Ketoprofen	4	6
Naproxen	2	4
Nonylphenol	3	4
Norfloxacin	3	4
Sulfamethoxazole	4	5
Tetracycline	2	4
Triclosan	2	2
Trimethoprim	2	4

A.5 Limitations of the Analysis

Due to the paucity of detailed matrix effects as well as degradation mechanism of TOrCs under direct and indirect UV photolysis, the UV254-based TOrC removals calculated in this study only considered light scattering and $^{\bullet}\text{OH}$ quenching of matrix by simply using an EBC, and neglected potential impact from by-products and interactions among matrix compounds with targets and by-products. Similarly, for sunlight process, UVA shading is the only matrix effect considered in the treated effluent, where indirect sunlight photolysis via ROS—e.g., $^{\bullet}\text{OH}$ and singlet oxygen as well as photo-excited DOMs may play an important role on attenuations of TOrCs under natural conditions.

Given the fact that adsorption isotherm constants can vary with adsorbent type and solution pH, PSDM-predicted sorptive removals may not be accurate enough to reflect TOrC relative attenuation during activated carbon processes without a consistent isotherm parameter database (Freundlich parameters used in this study obtained from the literature and represented over 15 different types of activated carbon and pH values ranging from 2.0 to 8.0). Besides, without comparing to experimentally-determined results, prediction accuracy of PSDM considering matrix effect still remains questionable since AdDesignTM simply utilizes empirical equations to manipulate Freundlich capacity parameter based on matrix and chemical types to represent fouling of adsorbent by NOM.

Additionally, the validity of applying the correlation obtained between the rejection results of 20 out of the 55 (< 40%) selected TOrCs and their molecular thickness data to estimate membrane treatment performance for the rest 35 compounds will remain unknown until additional experimental results are available.

The scoring system proposed in this study simply combines efficiencies of select processes independently neglecting potential influence of effluent quality/composition of each process on the following unit(s) in the treatment train. For instance, the aforementioned $\cdot\text{OH}$ quenching by background organic matter during UV/H₂O₂ AOP may lead to less fouling potential in the activated carbon process.

A.6 Conclusions

The remarkable effort of Grady (1990) on developing a systematic approach to rationalize engineered biotransformation of xenobiotic organic compounds during conventional wastewater treatment provided a heuristic guideline for scientists and engineers, stimulating broad-scale thinking relative to substantial environmental engineering problems. Besides the roles of available tools in reactor engineering, Grady emphasized the importance of databases of intrinsic kinetic parameters. Most importantly, Grady proposed that in most engineering applications, transformations of multiple xenobiotic compounds could be treated independently, using a single-substrate kinetic approach. This idea was followed up in the present study where removal efficiencies of 55 selected TOrCs were individually investigated in a single-substrate—i.e. a representative wastewater effluent during engineered (conventional and tertiary treatments) and natural processes using currently available tools. The potential relationships between treatment performance and compound physicochemical properties were tested to explore the physicochemical and biological determinants of TOrC removal efficiencies in a variety of engineered and natural processes, including one of the most common AOPs (H₂O₂ photolysis). Other common AOPs (e.g. Ozonation, TiO₂ catalysis,

Fenton's reactions) would need to be considered in a more thorough investigation of optimal treatment strategies.

It is apparent that simply utilizing QSAR calculated biodegradability (e.g. BioWin simulations) to estimate overall fate of TOrCs during conventional wastewater treatment is not absolutely reliable, which confirms observations reported previously (Rojas et al., 2013, and references therein).

All tertiary treatments which can be impacted by background organic matter present in the water matrix are capable of attenuating a broad spectrum of TOrCs, highly depending on compound's related physicochemical properties. Due to lack of good understanding of matrix effects as well as degradation mechanism of TOrCs during photon-driven tertiary treatment—e.g. UV-based advanced oxidation and sunlight photolysis, removals were simulated without considering the potential impact from by-products and interactions among matrix organics with targets and by-products. Even under these conditions, the effects of radical scavenging and light shading by organic matrix compounds have an important impact on TOrC treatment. Quantification of matrix interferences both in terms of physical effects (such as light absorption) and chemical effects (degradation mechanisms, radical scavenging, production of reactive oxygen species) remains a challenging key point in the evaluation of treatment technologies.

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APPENDIX A1: Supplementary Materials for APPENDIX A

Figure A1-1. Molecular structures and sizes of 1,4-DCB, 2,4-D, acetaminophen, anthracene, atrazine and benzo(a)pyrene obtained by using Materials Studio 4.0

Figure A1-2. Molecular structures and sizes of benzophenone, bezafibrate, bisphenol A, bromoxynil, caffeine and carbamazepine obtained by using Materials Studio 4.0

Figure A1-3. Molecular structures and sizes of carbofuran, chlorpyrifos, ciprofloxacin, clofibric acid, DEET and diazinon obtained by using Materials Studio 4.0

Figure A1-4. Molecular structures and sizes of diclofenac, diphenhydramine, diuron, doxycycline, E₁ and E₂ obtained by using Materials Studio 4.0

Figure A1-5. Molecular structures and sizes of E₃, EE₂, fluoranthene, gemfibrozil, ibuprofen and indomethacin obtained by using Materials Studio 4.0

Figure A1-6. Molecular structures and sizes of iopromide, ketoprofen, linuron, MCPA, mefenamic acid and metolachlor obtained by using Materials Studio 4.0

Figure A1-7. Molecular structures and sizes of metoprolol, naproxen, nonylphenol, norfloxacin, octylphenol and phenanthrene obtained by using Materials Studio 4.0

Figure A1-8. Molecular structures and sizes of phenol, progesterone, propachlor, pyrene, ranitidine and roxithromycin obtained by using Materials Studio 4.0

Figure A1-9. Molecular structures and sizes of simazine, sulfamerazine, sulfamethoxazole, testosterone, tetracycline and triclosan obtained by using Materials Studio 4.0

Figure A1-10. Molecular structure and size of trimethoprim obtained by using Materials Studio 4.0

Figure A1-11. Compound rejection rate as a function of NaCl rejection for acetaminophen, atrazine, bisphenol A and caffeine

Figure A1-12. Compound rejection rate as a function of NaCl rejection for carbamazepine, DEET, diclofenac and E₁

Figure A1-13. Compound rejection rate as a function of NaCl rejection for E₂, E₃, EE₂ and gemfibrozil

Figure A1-14. Compound rejection rate as a function of NaCl rejection for ibuprofen, ketoprofen, mefenamic acid and naproxen

Figure A1-15. Compound rejection rate as a function of NaCl rejection for progesterone, simazine, sulfamethoxazole and trimethoprim

Figure A1-16. Comparison of spectral absorbance of secondary effluent collected from Tres Rios Wastewater Reclamation Facility, Tucson, AZ and the ground level global solar spectral irradiances (at noon) at the University of Arizona, Tucson, Arizona, on June 12, 2015, obtained from SMARTS. The total organic carbon, pH and hardness of the effluent sample are 6.97 mg/L, 7.50 and 210 mg/L as CaCO₃.

Figure A1-17. BVF to breakthrough calculated by AdDesignSTM (PSDM) for 10 organic chemicals based on Freundlich isotherm parameters from an U.S. EPA (1980) report as a function of compound-specific $\log K_{ow}$. In all cases, $[\text{Chemicals}]_o = 10 \text{ nM}$. The Spearman correlation coefficient (ρ) is provided.

Figure A1-18. Compound rejection rate at NaCl rejection = 50% as a function of molecule length (A), molecule thickness (B) and $\log K_{ow}$ (C). Spearman correlation coefficients (ρ) are provided for each case.

Figure A1-19. Comparison of TOrCs removal efficiencies by direct low pressure UV and sunlight photolysis of 14 TOrCs in pure water. In all cases, $[TOrC]_0 = 10 \text{ nM}$.

Table A1-1. Summary of UV254-based photochemical parameters for the 55 TOrCs in this study.

CECs	Φ_{254} (mol/Ein)	ϵ_{254} (M ⁻¹ cm ⁻¹)	k _{OH} (M ⁻¹ s ⁻¹)	Reference
1,4-DCB			(5.40 ± 0.40)E+09	Kochany and Bolton 1992
	6.00E-01	1.18E+02	1.06E+10	Real et al. 2007a
2,4-D			2.33E+09	Armbrust 2000
			1.60E+09	Mabury and Crosby 1996
	9.50E-03	1.73E+02	5.00E+09	Haag and Yao 1992
Acetaminophen	(6.00 ± 2.00)E-03	7.80E+03	5.10E+09	Benitez et al. 2004b
	(1.80 ± 0.30)E-03	8.10E+03		Carlson et al. 2015
			9.70E+09	Rivas et al. 2011
		4.22E+03		Buxton et al. 1988
Anthracene	2.01E-01	1.04E+03		Kim et al. 2009
	9.60E-02	1.09E+03		Lehto et al. 2000
			(7.83 ± 4.21)E+09	Sanches et al. 2011
Atrazine	3.30E-02	3.68E+03		Kwok et al. 1994
			2.40E+09	Bolton and Stefan 2002
			1.70E+09	De Laat et al. 1994
			(2.60 ± 0.40)E+09	Chramosta et al. 1993
	5.00E-02	3.86E+03		Haag and Yao 1992
			2.10E+09	Nick et al. 1992
	6.00E-02	2.65E+03	7.30E+09	De Laat et al. 1996
		3.86E+03		Sanches et al. 2010
Benzo(a)pyrene	1.40E-02			Azrague and Osterhus 2009
			2.50E+10	Miller and Olejnik 2001
			2.53E+10	Miller et al. 2002
	3.14E-01	1.08E+03		Ledakowicz et al. 1999
				Sanches et al. 2011

Table A1-1. (Continued).

CECs	Φ_{254} (mol/Ein)	ϵ_{254} (M ⁻¹ cm ⁻¹)	k_{OH} (M ⁻¹ s ⁻¹)	Reference
Benzophenone			8.70E+09	Land 1968
			9.00E+09	Buxton et al. 1988
Bezafibrate			(7.40 ± 1.20)E+09	Huber et al. 2003
		9.50E+02	(8.00 ± 0.22)E+09	Razavi et al. 2009
Bisphenol A	8.50E-03		(1.02 ± 0.06)E+10	Rosenfeldt and Linden 2004
	(4.60 ± 0.43)E-03	7.50E+02	(5.80 ± 0.08)E+09	Baeza and Knappe 2011
Bromoxynil	4.00E-02	4.97E+03		Chelme-Ayala et al. 2010b
			(8.45 ± 0.40)E+09	Chelme-Ayala et al. 2010a
Caffeine	(1.80 ± 0.30)E-03	4.81E+03		Rivas et al. 2011
			6.90E+09	Kesavan and Powers 1985
			5.90E+09	Shi et al. 1991
Carbamazepine			(8.80 ± 1.20)E+09	Huber et al. 2003
			(9.40 ± 0.40)E+09	Lam and Mabury 2005
		6.03E+03	(2.05 ± 0.14)E+09	Vogna et al. 2004
		6.07E+03		Kim et al. 2009
	(6.00 ± 0.89)E-04	6.07E+03	(5.85 ± 0.09)E+09	Pereira et al. 2007
Carbofuran	1.66E-02	8.00E+02	1.73E+09	Benitez et al. 1995
Chlorpyrifos			4.17E+09	Armbrust 2000
	1.60E-02	6.50E+02		Wan et al. 1994
			(4.90 ± 0.10)E+09	Wu and Linden 2010
Ciprofloxacin	(1.03 ± 0.037)E-02	1.24E+04	(6.22 ± 0.001)E+09	Pereira et al. 2007
			(4.10 ± 0.30)E+09	Dodd et al. 2006
	(1.34 ± 0.32)E-02	2.20E+04	7.50E+09	Yuan et al. 2011
Clofibric acid	(5.39 ± 0.94)E-01	4.00E+02	(5.72 ± 0.02)E+09	Pereira et al. 2007
	(1.08 ± 0.02)E-02	3.80E+02	(2.38 ± 0.18)E+09	Andreozzi et al. 2003a

Table A1-1. (Continued).

CECs	Φ_{254} (mol/Ein)	ϵ_{254} (M ⁻¹ cm ⁻¹)	k_{OH} (M ⁻¹ s ⁻¹)	Reference
DEET		2.00E+03 1.21E+03	(4.70 ± 0.30)E+09	Packer et al. 2003
			(6.98 ± 0.12)E+09	Razavi et al. 2009
				Kim et al. 2009
			(4.95 ± 0.18)E+09	Song et al. 2009
Diazinon	8.20E-02	3.89E+03		Wan et al. 1994
	2.80E-02		8.40E+09	Real et al. 2007b
Diclofenac	(3.84 ± 0.32)E-02	2.00E+03	(9.00 ± 0.40)E+09	Shemer and Linden 2006
	(3.84 ± 0.75)E-01	(4.26 ± 0.13)E+03		Canonica et al. 2008
			(7.50 ± 1.50)E+09	Huber et al. 2003
	(21.3 ± 0.5)E-02	5.20E+03	(9.26 ± 0.26)E+09	Baeza and Knappe 2011
Diphenhydramine		3.47E+03		Kim et al. 2009
	(2.80 ± 0.20)E-01	(6.14 ± 0.08)E+03		Meite et al. 2010
			7.10E+09	Chen et al. 2009
	1.25E-01	3.88E+02	5.42E+09	Yuan et al. 2009
Diuron	1.15E-02	1.57E+04		Benitez et al. 2006
	(1.25 ± 0.05)E-02	(1.65 ± 0.05)E+04		Djebbar et al. 2003
			4.60E+09	De Laat et al. 1996
Doxycycline	1.90E-02	1.62E+04	1.27E+10	Sanches et al. 2010
	(1.10 ± 0.50)E-03	1.21E+04		Rivas et al. 2011
	(1.10 ± 0.20)E-03	1.22E+05	1.50E+09	Rivas et al. 2010a
	(2.19 ± 0.18)E-02	1.11E+04	7.74E+09	Yuan et al. 2011
E ₁		3.95E+02		Puma et al. 2010
	5.00E-04			Sarkar et al. 2014
E ₂	(3.50 ± 1.40)E-01	3.44E+02		Carlson et al. 2015
	(6.70 ± 0.70)E-02	(4.20 ± 0.20)E+02		Mazellier et al. 2008

Table A1-1. (Continued).

CECs	Φ_{254} (mol/Ein)	ϵ_{254} (M ⁻¹ cm ⁻¹)	$k_{\bullet OH}$ (M ⁻¹ s ⁻¹)	Reference
E ₃ EE ₂	4.30E-02		(1.41 ± 0.33)E+10	Rosenfeldt and Linden 2004
		3.86E+02		Puma et al. 2010
			(5.30 ± 0.40)E+09	Kosaka, et al. 2003
		2.34E+02		Puma et al. 2010
	(0.57 ± 0.06)E-01	(3.06 ± 0.28)E+03		Canonica et al. 2008
	(6.20 ± 0.70)E-02	(4.4 ± 0.35)E+02		Mazellier et al. 2008
Fluoranthene	2.60E-02		(1.08 ± 0.23)E+10	Rosenfeldt and Linden 2004
			(9.80 ± 1.20)E+09	Huber et al. 2003
		3.15E+02		Puma et al. 2010
	(8.00 ± 5.00)E-02	5.08E+02		Carlson et al. 2015
	5.47E-02	3.33E+02		Zhang et al. 2010
	4.47E-01	3.11E+02		Sanches et al. 2011
Gemfibrozil			1.76E+10	AopWin v1.92 Estimated ^a
Ibuprofen	(8.6 ± 1.2)E-02	3.45E+03	(1.00 ± 0.06)E+10	Razavi et al. 2009
Indomethacin		2.82E+02		Carlson et al. 2015
			(7.40 ± 1.20)E+09	Huber et al. 2003
			(6.50 ± 0.20)E+09	Packer et al. 2003
	1.92E-01	2.56E+02	6.67E+09	Yuan et al. 2009
Iopromide	(3.90 ± 0.40)E-02	1.48E+04		Kim et al. 2009
Ketoprofen		(2.10 ± 0.02)E+04	(3.30 ± 0.60)E+09	Canonica et al. 2008
		1.52E+04		Huber et al. 2003
	(2.36 ± 0.07)E-01	1.55E+04	(5.38 ± 0.07)E+09	Kim et al. 2009
Linuron	3.60E-01	1.52E+04	(8.40 ± 0.30)E+09	Pereira et al. 2007
	3.60E-02	1.34E+04		Real et al. 2009
				Benitez et al. 2006

Table A1-1. (Continued).

CECs	Φ_{254} (mol/Ein)	ϵ_{254} (M ⁻¹ cm ⁻¹)	k _{•OH} (M ⁻¹ s ⁻¹)	Reference
			4.30E+09	De Laat et al. 1996
	1.12E-03			Rao and Chu 2009
MCPA	1.49E-01	3.52E+02	6.60E+09	Benitez et al. 2004b
Mefenamic acid		4.63E+03		Kim et al. 2009
	(4.70 ± 1.40)E-03	5.50E+03	1.10E+10	Rivas et al. 2010a
Metolachlor			5.10E+09	De Laat et al. 1996
	6.10E-01	6.24E+02		Benitez et al. 2004a
			(6.70 ± 0.40)E+09	Acero et al. 2003
	(3.02 ± 0.01)E-01	5.03E+02	(9.07 ± 0.21)E+09	Wu et al. 2007
Metoprolol		2.35E+02		Kim et al. 2009
	6.38E-02	9.00E+02	(6.83 ± 0.47)E+09	Benitez et al. 2009
	5.60E-03	(5.60 ± 0.12)E+02		Rivas et al. 2010b
			(7.30 ± 0.20)E+09	Benner et al. 2008
			(8.39 ± 0.06)E+09	Song et al. 2008
Naproxen		3.96E+03		Kim et al. 2009
	(9.30 ± 0.27)E-03	4.90E+03	(8.61 ± 0.002)E+09	Pereira et al. 2007
			(9.60 ± 0.50)E+09	Packer et al. 2003
	(2.40 ± 0.50)E-02	(3.95 ± 0.04)E+03		Meite et al. 2010
	4.98E-02	3.20E+03	(8.37 ± 0.61)E+09	Benitez et al. 2009
Nonylphenol	(2.43 ± 1.57)E-01	4.00E+02		Carlson et al. 2015
			(1.10 ± 0.20)E+10	Ning et al. 2007
Norfloxacin	(3.40 ± 0.30)E-03	1.60E+04	1.00E+09	Rivas et al. 2010a
Octylphenol			(1.40 ± 0.20)E+10	Ning et al. 2007
Phenanthrene	(6.90 ± 0.50)E-03	4.05E+04		Beltrán, et al. 1995
			1.34E+10	Beltrán, et al. 1996

Table A1-1. (Continued).

CECs	Φ_{254} (mol/Ein)	ϵ_{254} (M ⁻¹ cm ⁻¹)	k_{OH} (M ⁻¹ s ⁻¹)	Reference
Phenol	2.10E-02	9.80E+02	(1.40 ± 0.30)E+10	Wan et al. 1994
			5.10E+09	Land and Ebert 1967
			6.60E+09	Anbar et al. 1966
	(3.00 ± 0.50)E-02	(5.20 ± 0.10)E+02		Field et al. 1982
Progesterone	(2.20 ± 0.50)E-02	(1.70 ± 0.04)E+04		Zamy et al. 2004
			(8.50 ± 0.90)E+08	Meite et al. 2010
Propachlor	(1.27 ± 0.10)E-01	4.21E+02		Mezyk et al. 2010
			(4.60 ± 0.30)E+09	Benitez et al. 2004a
			4.30E+09	Acero et al. 2003
Pyrene	3.85E-03	1.82E+04		De Laat et al. 1996
Ranitidine			(1.50 ± 0.20)E+10	Lehto et al. 2000
Roxithromycin			(5.40 ± 0.30)E+09	Latch et al. 2003a
Simazine			2.10E+09	Dodd et al. 2006
	8.30E-02	3.33E+03		Chramosta et al. 1993
			(2.80 ± 0.20)E+09	Nick et al. 1992
Sulfamerazine			(7.80 ± 0.30)E+09	Haag and Yao 1992
Sulfamethoxazole	(4.60 ± 2.10)E-02	(1.68 ± 0.04)E+04		Mezyk et al. 2008
			(5.50 ± 0.70)E+09	Canonica et al. 2008
	(3.30 ± 0.40)E-02	1.71E+04		Huber et al. 2003
	(2.97 ± 0.09)E-02	1.66E+04	5.56E+09	Carlson et al. 2015
			(3.70 ± 0.10)E+09	Baeza and Knappe 2011
		7.35E+03		Lam and Mabury 2005
			(5.80 ± 0.20)E+09	Kim et al. 2009
		1.19E+04		Boreen et al. 2004
				Azrague and Osterhus 2009

Table A1-1. (Continued).

CECs	Φ_{254} (mol/Ein)	ϵ_{254} (M ⁻¹ cm ⁻¹)	$k_{\bullet\text{OH}}$ (M ⁻¹ s ⁻¹)	Reference
Testosterone	(3.30 ± 0.50)E-02 2.25E-01	(1.51 ± 0.08)E+04	(8.50 ± 0.30)E+09	Mezyk et al. 2008 Meite et al. 2010 Vulliet et al. 2010
Tetracycline		4.11E+03	(7.70 ± 1.20)E+09	Kim et al. 2009 Dodd et al. 2006
Triclosan	3.80E-03 (3.40 ± 0.70)E-01	(1.35 ± 0.006)E+04 1.80E+03	5.49E+09 (5.40 ± 0.30)E+09	López-Peñalver et al. 2010 Carlson et al. 2015 Sirés et al. 2007
Trimethoprim	(1.18 ± 0.11)E-03	4.07E+03 2.94E+03	(5.70 ± 0.30)E+09 (6.90 ± 0.20)E+09 8.66E+09	Latch et al. 2005 Carlson et al. 2015 Baeza and Knappe 2011 Dodd et al. 2006 Luo et al. 2012

^a AopWin v1.92 was embedded in the EPI SuiteTM (v4.11).

Table A1-2. Summary of TOrCs sunlight and simulated sunlight quantum yields.

TOrCs	Φ_{Sunlight} (mol/Ein)	$\Phi_{\text{Simulated Sunlight}}$ (mol/Ein)	Reference
1,4-DCB	1.70E-02		Mansour and Feicht 1994
Acetaminophen	2.40E-01 – 4.50E-01		Yamamoto et al. 2009
Carbamazepine	4.77E-05		Andreozzi et al. 2003b
	6.00E-06 – 2.70E-05		Yamamoto et al. 2009
Clofibric acid	2.00E-03		Packer et al. 2003
	5.53E-03		Andreozzi et al. 2003b
Diclofenac	9.40E-02		Packer et al. 2003
	3.75E-02		Andreozzi et al. 2003b
E ₁		2.96E-02	Lin and Reinhard 2005
E ₂		4.80E-03	Lin and Reinhard 2005
E ₃		4.80E-03	Lin and Reinhard 2005
EE ₂		4.80E-03	Lin and Reinhard 2005
Ibuprofen	ND		Packer et al. 2003
	3.00E-05 – 4.20E-04		Yamamoto et al. 2009
Indomethacin	3.90E-04 – 4.70E-04		Yamamoto et al. 2009
Mefenamic acid	1.10E-05 – 7.50E-05		Yamamoto et al. 2009
	1.50E-04		Werner et al. 2005
Naproxen	3.60E-02		Packer et al. 2003
		2.60E-02	Lin and Reinhard 2005
Nonylphenol		3.00E-03	Neamțu and Frimmel 2006
Norfloxacin		4.30E-02	Wammer et al. 2013
Ranitidine	5.30E-03 ± 5.00E-04		Latch et al. 2003a
Roxithromycin		2.00E-04	Batchu et al. 2014
Sulfamethoxazole	5.00E-01		Boreen et al. 2004
		1.08E+00	Batchu et al. 2014
Testosterone	3.27E-02 – 5.20E-02		Young et al. 2013
Triclosan	4.00E-02		Latch et al. 2003b

Note: ND = Not detected.

Table A1-3. Summary of Freundlich isotherm information of 43 TOrCs.

TOrCs	K (mg/g)(L/mg) ^{1/n}	1/n	Adsorbent Type	Adsorbent Details	pH	Ref.
1,4-DCB	121	0.47	Activated carbon	Calgon F300	5.10	U.S. EPA 1980
2,4-D	43.9	0.34	Activated carbon	Sigma C-5510	2.00	Aksu and Kabasakal 2005
Acetaminophen	153	0.35	Activated carbon	Calgon F400	NM	Chang et al. 2015
Anthracene	376	0.70	Activated carbon	Calgon F300	5.30	U.S. EPA 1980
Atrazine	289	0.29	Activated carbon	Calgon F400	NM	Speth and Miltner 1990
Benzo(a)pyrene	33.6	0.44	Activated carbon	Calgon F300	7.10	U.S. EPA 1980
Bezafibrate	141	0.19	Activated carbon	Pulverized granular activated carbon based on coal	NM	Ternes et al. 2002
Bisphenol A	20.7	0.18	Activated carbon	Derived from Empty Fruit Bunch	7.00	Wirasnita et al. 2014
Bromoxynil	201	0.18	Activated carbon	F400 provided by Chemviron	NM	Baup et al. 2000
Caffeine	239	0.04	Activated carbon	Calgon F400	NM	Sotelo et al. 2012
Carbamazepine	430.	0.38	Activated carbon	Pulverized granular activated carbon based on coal	NM	Ternes et al. 2002
Carbofuran	266	0.41	Activated carbon	Calgon F300	NM	U.S. DA 2001
Chlorpyrifos	11.3	0.70	Activated carbon	Powdered activated carbon from Adwic	NM	Alalm et al. 2015
Ciprofloxacin	32.2	0.45	Activated carbon	Calgon	7.00	Zhu et al. 2015
Clofibric acid	71.0	0.25	Activated carbon	Pulverized granular activated carbon based on coal	NM	Ternes et al. 2002
Diazinon	3.63	0.33	Activated carbon	Powdered activated carbon from Adwic	NM	Alalm et al. 2015
Diclofenac	304	0.08	Activated carbon	Calgon F400	NM	Chang et al. 2015
Diphenhydramine	95.7	0.80	Activated carbon	Powdered activated carbon from WPH	8.00	Hanigan et al. 2012

Table A1-3. (Continued).

TOrCs	K (mg/g)(L/mg) ^{1/n}	1/n	Adsorbent Type	Adsorbent Details	pH	Ref.
Diuron	279	0.22	Activated carbon	F400 provided by Chemviron	NM	Baup et al. 2000
E ₁	610.	0.41	Activated carbon	Coconut shell made activated carbon	NM	Fukuhara et al. 2006
E ₂	2.65	0.33	Activated carbon	Jacobi Carbons	7.00	Ifelebuegu 2012
E ₃	0.31	0.78	Activated charcoal	Granular activated charcoal from Loba Chemie Pvt. Ltd.	7.00	Kumar et al. 2012
EE ₂	2.15	0.28	Activated carbon	Jacobi Carbons	7.00	Ifelebuegu 2012
Fluoranthene	664	0.61	Activated carbon	Calgon F300	5.30	U.S. EPA 1980
Ibuprofen	122	0.17	Activated carbon	F400 provided by Chemviron	7.40	Delgado et al. 2015
Iopromide	71.7	0.30	Activated carbon	Powdered activated carbon from Dongyang Carbon Co.	6.00	Kim et al. 2014
Ketoprofen	1.14	0.23	Activated carbon	Activated carbon prepared from agricultural by-product	4.10	Baccar et al. 2012
Linuron	159	0.23	Activated carbon	NM	NM	Zahoor 2013
MCPA	29.5	0.29	Activated carbon	Aquacarb 208A from Waterlink Sutcliffe Carbons	7.00	Gimeno et al. 2003
Mefenamic acid	9.54	0.59	Activated charcoal	NM	8.00	Khalaf et al. 2013
Metolachlor	233	0.13	Activated carbon	Calgon F400	NM	Speth and Miltner 1990
Naproxen	12.1	0.37	Activated carbon	Calgon F400	NM	Yu et al. 2008
Nonylphenol	250.	0.37	Activated carbon	Calgon F300	7.00	U.S. EPA 1980
Norfloxacin	300.	0.17	Activated carbon	Activated carbon developed from Trapa natans husk	7.50	Xie et al. 2011
Phenanthrene	215	0.44	Activated carbon	Calgon F300	5.30	U.S. EPA 1980
Phenol	21	0.54	Activated carbon	Calgon F300	7.00	U.S. EPA 1980

Table A1-3. (Continued).

TOrCs	K (mg/g)(L/mg) ^{1/n}	1/n	Adsorbent Type	Adsorbent Details	pH	Ref.
Pyrene	389	0.39	Activated carbon	Calgon F400	7.00	Walters and Luthy1984
Ranitidine	404	0.21	Activated carbon	Powdered activated carbon from WPH	8.00	Hanigan et al. 2012
Simazine	150.	0.23	Activated carbon	Calgon F400	NM	Speth and Miltner 1990
Sulfamethoxazole	227	0.22	Activated carbon	Calgon F400	NM	Chang et al. 2015
Tetracycline	105	0.56	Activated carbon	Powdered activated carbon from WPH	8.00	Hanigan et al. 2012
Triclosan	3.03	0.62	Activated carbon	Powdered activated carbon from DC Chemical Co. Ltd., Seoul, Korea	7.00	Behera et al. 2010
Trimethoprim	142	0.18	Activated carbon	Powdered activated carbon from James Cumming & Sons Pty Ltd.	4.00	Kim et al. 2010

Note: NM = Not mentioned.

Table A1-4. Summary of reported compound-specific separation efficiencies for 20 selected TOxCs.

TOxCs	TOxCs Rejection %	Filtration Type (Membrane Details)	NaCl Rejection %	Reference
Acetaminophen	92.2	RO (X20)	99.5	Comerton et al. 2008
	99.9	NF (NE404090)	95	Kim et al. 2007
	99.9	RO (RE4040FL)	99.6	Kim et al. 2007
	45	NF (NF90-400)	90	Radjenović et al. 2008
	60	RO (BW30LE-440)	99	Radjenović et al. 2008
	85	RO (BW30LE-440)	99	Radjenović et al. 2008
	23	NF (NF200)	72	Yangali-Quintanilla et al. 2010
	72.7	RO (BW30LE)	99	Yangali-Quintanilla et al. 2010
	76.5	NF (NF90)	90	Yangali-Quintanilla et al. 2010
	94.3	RO (BW30-400-FR)	99.5	Huang et al. 2011
Atrazine	61.4	BF (HNF-1)	35	Kiso et al. 2002
	73.4	NF (NF270)	45	Alturki et al. 2010
	94.1	RO (BW30)	97.7	Alturki et al. 2010
	95.9	NF (NF90)	85	Alturki et al. 2010
	99.1	RO (ESPA2)	96.5	Alturki et al. 2010
	10.9	NF (sulfonated polyethersulfone)	15	Kiso et al. 2000
	14.9	NF (sulfonated polyethersulfone)	51	Kiso et al. 2000
	68.4	NF (poly(vinyl alcohol)/polyamide)	60	Kiso et al. 2000
	97.5	NF (poly(vinyl alcohol)/polyamide)	92	Kiso et al. 2000
Bisphenol A	83	RO (XLE)	90	Kimura et al. 2004
	96.1	RO (X20)	99.5	Comerton et al. 2008
	45	NF (ESNA)	77	Kimura et al. 2003
	99	RO (XLE)	99	Kimura et al. 2003
	38.9	NF (NF270)	45	Alturki et al. 2010
	72.2	RO (ESPA2)	96.5	Alturki et al. 2010

Table A1-4. (Continued).

TOrCs	TOrCs Rejection %	Filtration Type (Membrane Details)	NaCl Rejection %	Reference
Caffeine	77.8	NF (NF90)	85	Alturki et al. 2010
	77.8	RO (BW30)	97.7	Alturki et al. 2010
	57.5	NF (NF200)	72	Yangali-Quintanilla et al. 2010
	89.5	NF (NF90)	90	Yangali-Quintanilla et al. 2010
	95	RO (ESPA2)	99.5	Yangali-Quintanilla et al. 2010
	98.4	RO (BW30-400-FR)	99.5	Huang et al. 2011
	70	RO (XLE)	90	Kimura et al. 2004
	94.7	RO (X20)	99.5	Comerton et al. 2008
	83.3	RO (TFE-HR)	99.55	Snyder et al. 2007
	99.8	NF (NE404090)	95	Kim et al. 2007
	99.8	RO (RE4040FL)	99.6	Kim et al. 2007
	73	NF (NF270)	45	Alturki et al. 2010
	91.2	NF (NF90)	85	Alturki et al. 2010
	91.2	RO (BW30)	97.7	Alturki et al. 2010
	97.6	RO (ESPA2)	96.5	Alturki et al. 2010
	75	RO	99	Sui et al. 2010
	68	NF (NF200)	72	Yangali-Quintanilla et al. 2010
	90	RO (ESPA2)	99.5	Yangali-Quintanilla et al. 2010
	91.5	NF (NF90)	90	Yangali-Quintanilla et al. 2010
	98.4	RO (BW30-400-FR)	99.5	Huang et al. 2011
Carbamazepine	100	RO (TR70-4021-HF)	99.4	Dolar et al. 2012b
	85	RO (SC-3100)	94	Kimura et al. 2004
	91	RO (XLE)	90	Kimura et al. 2004
	91.5	RO (X20)	99.5	Comerton et al. 2008
	97.6	NF (NE404090)	95	Kim et al. 2007

Table A1-4. (Continued).

TOrCs	TOrCs Rejection %	Filtration Type (Membrane Details)	NaCl Rejection %	Reference
DEET	97.6	RO (RE4040FL)	99.6	Kim et al. 2007
	73.1	NF (NF270)	45	Alturki et al. 2010
	92	RO (BW30)	97.7	Alturki et al. 2010
	97.1	NF (NF90)	85	Alturki et al. 2010
	98.9	RO (ESPA2)	96.5	Alturki et al. 2010
	69	NF (NF270)	52.5	Gur-Reznik et al. 2011
	98	RO (SW30)	99.4	Gur-Reznik et al. 2011
	98	RO (BW30)	99.5	Gur-Reznik et al. 2011
	98	NF (NF90-400)	85-95	Radjenović et al. 2008
	99	RO (BW30LE-440)	99	Radjenović et al. 2008
	100	RO (BW30LE-440)	99	Radjenović et al. 2008
	90	NF (UTC-60)	55	Kimura et al. 2009
	100	RO (LF10)	98.9	Kimura et al. 2009
	90	RO	99	Sui et al. 2010
	82.5	NF (NF200)	72	Yangali-Quintanilla et al. 2010
	91	NF (NF90)	90	Yangali-Quintanilla et al. 2010
	95	RO (ESPA2)	99.5	Yangali-Quintanilla et al. 2010
	99	RO (BW30LE)	99	Yangali-Quintanilla et al. 2010
	98.2	RO (BW30-400-FR)	99.5	Huang et al. 2011
	96.1	RO (X20)	99.5	Comerton et al. 2008
	94.4	NF (NE404090)	95	Kim et al. 2007
	94.4	RO (RE4040FL)	99.6	Kim et al. 2007
	67.3	NF (NF270)	45	Alturki et al. 2010
	90	NF (NF90)	85	Alturki et al. 2010
	90.7	RO (BW30)	97.7	Alturki et al. 2010

Table A1-4. (Continued).

TOrCs	TOrCs Rejection %	Filtration Type (Membrane Details)	NaCl Rejection %	Reference
Diclofenac	96	RO (ESPA2)	96.5	Alturki et al. 2010
	90	RO	99	Sui et al. 2010
	93	NF (ESNA)	77	Kimura et al. 2003
	95	RO (XLE)	99	Kimura et al. 2003
	90	NF (NE404090)	95	Kim et al. 2007
	90	RO (RE4040FL)	99.6	Kim et al. 2007
	91	NF (NF270)	45	Alturki et al. 2010
	91	NF (NF90)	85	Alturki et al. 2010
	91	RO (BW30)	97.7	Alturki et al. 2010
	91	RO (ESPA2)	96.5	Alturki et al. 2010
	100	NF (NF90-400)	90	Radjenović et al. 2008
	100	RO (BW30LE-440)	99	Radjenović et al. 2008
	100	RO (BW30LE-440)	99	Radjenović et al. 2008
	99.4	RO (LF10)	98.9	Kimura et al. 2009
E ₁	90	RO	99	Sui et al. 2010
	96.9	RO (X20)	99.5	Comerton et al. 2008
	85	RO (TFE-HR)	99.55	Snyder et al. 2007
	68	NF (NF270)	45	Alturki et al. 2010
	68	NF (NF90)	85	Alturki et al. 2010
	68	RO (BW30)	97.7	Alturki et al. 2010
	68	RO (ESPA2)	96.5	Alturki et al. 2010
	82	NF (NF200)	72	Yangali-Quintanilla et al. 2010
	92.5	NF (NF90)	90	Yangali-Quintanilla et al. 2010
	92.5	NF (NF-270)	40	Nghiem et al. 2004
	95	NF (NF-90)	85	Nghiem et al. 2004

Table A1-4. (Continued).

TOrCs	TOrCs Rejection %	Filtration Type (Membrane Details)	NaCl Rejection %	Reference
E ₂	63	NF (NF-DS5DK)	96	Dudziak and Bodzek 2009
	78.6	NF (NF-SF10)	73	Dudziak and Bodzek 2009
	83	RO (XLE)	90	Kimura et al. 2004
	95.6	RO (X20)	99.5	Comerton et al. 2008
	80	RO (TFE-HR)	99.55	Snyder et al. 2007
	92.5	NF (NF-90)	85	Nghiem et al. 2004
	92.5	NF (NF-270)	40	Nghiem et al. 2004
E ₃	76.7	NF (NF-DS5DK)	96	Dudziak and Bodzek 2009
	86.8	NF (NF-SF10)	73	Dudziak and Bodzek 2009
	95.2	RO (X20)	99.5	Comerton et al. 2008
	80.5	RO (TFE-HR)	99.55	Snyder et al. 2007
	98.4	NF (NE404090)	95	Kim et al. 2007
	98.4	RO (RE4040FL)	99.6	Kim et al. 2007
	71.1	NF (NF-DS5DK)	96	Dudziak and Bodzek 2009
EE ₂	79.8	NF (NF-SF10)	73	Dudziak and Bodzek 2009
	97.1	RO (X20)	99.5	Comerton et al. 2008
	80	RO (TFE-HR)	99.55	Snyder et al. 2007
	92	NF (NF270)	45	Alturki et al. 2010
	93	NF (NF90)	85	Alturki et al. 2010
	93	RO (BW30)	97.7	Alturki et al. 2010
	93	RO (ESPA2)	96.5	Alturki et al. 2010
	90	NF (NF200)	72	Yangali-Quintanilla et al. 2010
	92	NF (NF90)	90	Yangali-Quintanilla et al. 2010
	95	RO (BW30LE)	99	Yangali-Quintanilla et al. 2010
	97.9	RO (BW30-400-FR)	99.5	Huang et al. 2011

Table A1-4. (Continued).

TOrCs	TOrCs Rejection %	Filtration Type (Membrane Details)	NaCl Rejection %	Reference
Gemfibrozil	90.4	NF (NF-DS5DK)	96	Dudziak and Bodzek 2009
	93.6	NF (NF-SF10)	73	Dudziak and Bodzek 2009
	96.9	RO (X20)	99.5	Comerton et al. 2008
	89	RO (TFE-HR)	99.55	Snyder et al. 2007
	50	RO (BW30LE-440)	99	Radjenović et al. 2008
	53	NF (NF90-400)	90	Radjenović et al. 2008
	92	RO (BW30LE-440)	99	Radjenović et al. 2008
	90	RO	99	Sui et al. 2010
	91	NF (NF200)	72	Yangali-Quintanilla et al. 2010
	96	NF (NF90)	90	Yangali-Quintanilla et al. 2010
Ibuprofen	100	RO (ESPA2)	99.5	Yangali-Quintanilla et al. 2010
	99.9	RO (BW30-400-FR)	99.5	Huang et al. 2011
	90.3	RO (TFE-HR)	99.55	Snyder et al. 2007
	99.9	NF (NE404090)	95	Kim et al. 2007
	99.9	RO (RE4040FL)	99.6	Kim et al. 2007
	64.4	NF (NF270)	45	Alturki et al. 2010
	64.4	NF (NF90)	85	Alturki et al. 2010
	64.4	RO (BW30)	97.7	Alturki et al. 2010
	64.4	RO (ESPA2)	96.5	Alturki et al. 2010
	89	NF (NF200)	72	Yangali-Quintanilla et al. 2010
Ketoprofen	96.5	NF (NF90)	90	Yangali-Quintanilla et al. 2010
	99	RO (ESPA2)	99.5	Yangali-Quintanilla et al. 2010
	97.9	RO (BW30-400-FR)	99.5	Huang et al. 2011
	96	NF (NF270)	45	Alturki et al. 2010
	96	NF (NF90)	85	Alturki et al. 2010

Table A1-4. (Continued).

TOrCs	TOrCs Rejection %	Filtration Type (Membrane Details)	NaCl Rejection %	Reference
Mefenamic acid	96	RO (BW30)	97.7	Alturki et al. 2010
	96	RO (ESPA2)	96.5	Alturki et al. 2010
	85	RO (BW30LE-440)	99	Radjenović et al. 2008
	97	NF (NF90-400)	90	Radjenović et al. 2008
	98	RO (BW30LE-440)	99	Radjenović et al. 2008
	100	RO (LF10)	98.9	Kimura et al. 2009
	91.5	NF (NF200)	72	Yangali-Quintanilla et al. 2010
	95	NF (NF90)	90	Yangali-Quintanilla et al. 2010
	98	RO (BW30LE)	99	Yangali-Quintanilla et al. 2010
	100	RO (ESPA2)	99.5	Yangali-Quintanilla et al. 2010
	30	NF (NF90-400)	90	Radjenović et al. 2008
	45	RO (BW30LE-440)	99	Radjenović et al. 2008
	71	RO (BW30LE-440)	99	Radjenović et al. 2008
	71.3	NF (UTC-60)	55	Kimura et al. 2009
	98.4	RO (LF10)	98.9	Kimura et al. 2009
Naproxen	25	RO	99	Sui et al. 2010
	78.8	RO (TFE-HR)	99.55	Kim et al. 2007
	99.6	NF (NE404090)	95	Kim et al. 2007
	97.9	NF (NF270)	45	Alturki et al. 2010
	98.8	RO (BW30)	97.7	Alturki et al. 2010
	99	NF (NF90)	85	Alturki et al. 2010
	99	RO (ESPA2)	96.5	Alturki et al. 2010
	91.5	NF (NF200)	72	Yangali-Quintanilla et al. 2010
	95	NF (NF90)	90	Yangali-Quintanilla et al. 2010
	100	RO (ESPA2)	99.5	Yangali-Quintanilla et al. 2010

Table A1-4. (Continued).

TOrCs	TOrCs Rejection %	Filtration Type (Membrane Details)	NaCl Rejection %	Reference
Progesterone	94.5	RO (BW30-400-FR)	99.5	Huang et al. 2011
	96	NF(NF-270)	40	Nghiem et al. 2004
	96.5	NF (NF-90)	85	Nghiem et al. 2004
	79.4	NF (NF-DS5DK)	96	Dudziak and Bodzek 2009
	89.1	NF (NF-SF10)	73	Dudziak and Bodzek 2009
Simazine	42.2	NF (HNF-1)	35	Kiso et al. 2002
	6.4	NF (sulfonated polyethersulfone)	15	Kiso et al. 2000
	9.15	NF (sulfonated polyethersulfone)	51	Kiso et al. 2000
	59.6	NF (poly(vinyl alcohol)/polyamide)	60	Kiso et al. 2000
	98.6	NF (poly(vinyl alcohol)/polyamide)	92	Kiso et al. 2000
Sulfamethoxazole	15	NF (NF270)	13.6	Dolar et al. 2012a
	24	RO/NF (HL)	27.1	Dolar et al. 2012a
	29	NF	24.6	Dolar et al. 2012a
	96	RO (LFC-1)	96.5	Dolar et al. 2012a
	96	RO (XLE)	89.5	Dolar et al. 2012a
	96	NF (NF90)	89.9	Dolar et al. 2012a
	98	RO (TR70-4021-HF)	99.4	Dolar et al. 2012b
	95.6	RO (X20)	99.5	Comerton et al. 2008
	89	NF (NF270)	45	Alturki et al. 2010
	89	NF (NF90)	85	Alturki et al. 2010
	89	RO (BW30)	97.7	Alturki et al. 2010
	89	RO (ESPA2)	96.5	Alturki et al. 2010
	84	NF (NF200)	72	Yangali-Quintanilla et al. 2010
	95.5	NF (NF90)	90	Yangali-Quintanilla et al. 2010
	100	RO (BW30LE)	99	Yangali-Quintanilla et al. 2010

Table A1-4. (Continued).

TOrCs	TOrCs Rejection %	Filtration Type (Membrane Details)	NaCl Rejection %	Reference
Trimethoprim	92.5	RO (BW30-400-FR)	99.5	Huang et al. 2011
	66	RO/NF (HL)	27.1	Dolar et al. 2012a
	68	NF (NF270)	13.6	Dolar et al. 2012a
	82	NF	24.6	Dolar et al. 2012a
	95	RO (XLE)	89.5	Dolar et al. 2012a
	98	RO (LFC-1)	96.5	Dolar et al. 2012a
	98	NF (NF90)	89.9	Dolar et al. 2012a
	90.6	RO (TFE-HR)	99.55	Snyder et al. 2007
	95.2	NF (NE404090)	95	Kim et al. 2007
	95.2	RO (RE4040FL)	99.6	Kim et al. 2007
	78.3	NF (NF270)	45	Alturki et al. 2010
	93.4	RO (BW30)	97.7	Alturki et al. 2010
	96.7	NF (NF90)	85	Alturki et al. 2010
	99	RO (ESPA2)	96.5	Alturki et al. 2010
	90	RO	99	Sui et al. 2010
	87.1	RO (BW30-400-FR)	99.5	Huang et al. 2011

Table A1-5. Summary of TOrCs molar absorptivity from 300 to 400 nm.

λ (nm)	Molar Absorptivity ($M^{-1}cm^{-1}$)					
	Acetaminophen ^a	Carbamazepine ^b	Diclofenac ^c	E ₁ ^d	E ₂ ^e	EE ₂ ^f
300	4.30E+02	9.30E+03	4.10E+03	1.78E+03	3.28E+03	3.80E+02
305	3.00E+02	6.98E+03	2.70E+03	1.39E+03	2.37E+03	3.09E+02
310	2.20E+02	4.82E+03	1.60E+03	7.50E+02	2.00E+03	2.86E+02
315	2.20E+02	3.08E+03	7.00E+02	2.30E+02	1.82E+03	2.36E+02
320	2.20E+02	1.75E+03	2.50E+02	2.00E+01	1.64E+03	2.00E+02
325	2.20E+02	1.20E+03	5.00E+01	1.00E-03	1.27E+03	2.08E+02
330	2.20E+02	3.50E+02	1.00E-03	1.00E-03	1.09E+03	1.93E+02
335	2.20E+02	1.00E-03	1.00E-03	1.00E-03	1.00E+03	1.82E+02
340	2.20E+02	1.00E-03	1.00E-03	1.00E-03	9.10E+02	2.00E+02
345	2.20E+02	1.00E-03	1.00E-03	1.00E-03	7.28E+02	1.52E+02
350	2.20E+02	1.00E-03	1.00E-03	1.00E-03	5.46E+02	1.80E+02
355	2.20E+02	1.00E-03	1.00E-03	1.00E-03	3.64E+02	1.80E+02
360	2.20E+02	1.00E-03	1.00E-03	1.00E-03	1.82E+02	1.47E+02
365	2.20E+02	1.00E-03	1.00E-03	1.00E-03	1.00E-03	1.39E+02
370	2.20E+02	1.00E-03	1.00E-03	1.00E-03	1.00E-03	1.27E+02
375	2.20E+02	1.00E-03	1.00E-03	1.00E-03	1.00E-03	1.14E+02
380	2.20E+02	1.00E-03	1.00E-03	1.00E-03	1.00E-03	1.01E+02
385	2.20E+02	1.00E-03	1.00E-03	1.00E-03	1.00E-03	8.87E+01
390	2.20E+02	1.00E-03	1.00E-03	1.00E-03	1.00E-03	8.87E+01
395	2.20E+02	1.00E-03	1.00E-03	1.00E-03	1.00E-03	7.60E+01
400	2.20E+02	1.00E-03	1.00E-03	1.00E-03	1.00E-03	7.60E+01

Table A1-5. (Continued).

λ (nm)	Molar Absorptivity ($M^{-1}cm^{-1}$)					
	Ibuprofen ^b	Indomethacin ^{b,g}	Mefenamic acid ^h	Naproxen ^d	Nonylphenol ^e	Norfloxacin ⁱ
300	6.98E+03	6.25E+03	8.35E+03	1.00E+02	2.64E+01	2.12E+04
305	5.05E+03	5.98E+03	7.00E+03	2.00E+02	1.91E+01	2.08E+04
310	4.02E+03	6.20E+03	5.70E+03	3.90E+02	1.61E+01	2.17E+04
315	4.30E+03	6.52E+03	4.70E+03	7.00E+02	1.47E+01	2.33E+04
320	3.70E+03	6.58E+03	4.35E+03	6.80E+02	1.32E+01	2.40E+04
325	1.68E+03	6.55E+03	4.45E+03	7.10E+02	1.03E+01	2.37E+04
330	7.20E+02	5.50E+03	4.70E+03	1.01E+03	8.81E+00	2.27E+04
335	1.00E-03	5.06E+03	4.75E+03	6.00E+02	8.07E+00	2.13E+04
340	1.00E-03	4.63E+03	4.70E+03	5.00E+01	7.34E+00	1.80E+04
345	1.00E-03	4.19E+03	4.35E+03	1.00E-03	5.87E+00	1.07E+04
350	1.00E-03	3.75E+03	3.80E+03	1.00E-03	4.40E+00	7.33E+03
355	1.00E-03	3.32E+03	3.20E+03	1.00E-03	2.94E+00	5.00E+03
360	1.00E-03	2.88E+03	2.50E+03	1.00E-03	1.47E+00	3.60E+03
365	1.00E-03	2.44E+03	1.75E+03	1.00E-03	1.00E-03	2.67E+03
370	1.00E-03	2.00E+03	1.15E+03	1.00E-03	1.00E-03	2.00E+03
375	1.00E-03	1.03E+03	7.00E+02	1.00E-03	1.00E-03	1.40E+03
380	1.00E-03	1.80E+03	4.00E+02	1.00E-03	1.00E-03	1.00E+03
385	1.00E-03	1.80E+03	2.50E+02	1.00E-03	1.00E-03	7.33E+02
390	1.00E-03	1.80E+03	1.50E+02	1.00E-03	1.00E-03	6.67E+02
395	1.00E-03	1.80E+03	7.50E+01	1.00E-03	1.00E-03	3.33E+02
400	1.00E-03	1.80E+03	1.00E-03	1.00E-03	1.00E-03	1.33E+02

Table A1-5. (Continued).

λ (nm)	Molar Absorptivity ($M^{-1}cm^{-1}$)				
	Ranitidine ^j	Roxithromycin ^k	Sulfamethoxazole ^k	Testosterone ^l	Triclosan ^e
300	1.38E+04	1.67E+04	6.36E+03	7.87E+01	1.13E+02
305	1.50E+04	1.58E+04	5.62E+03	8.23E+01	6.76E+01
310	1.59E+04	1.55E+04	5.07E+03	8.24E+01	4.13E+01
315	1.59E+04	1.54E+04	4.79E+03	8.12E+01	3.76E+01
320	1.52E+04	1.52E+04	4.61E+03	7.58E+01	3.38E+01
325	1.31E+04	1.43E+04	4.51E+03	6.78E+01	2.63E+01
330	1.03E+04	1.46E+04	4.41E+03	5.80E+01	2.25E+01
335	7.60E+03	1.25E+04	4.31E+03	4.50E+01	2.07E+01
340	5.30E+03	1.25E+04	4.21E+03	3.39E+01	1.88E+01
345	2.90E+03	1.22E+04	4.12E+03	2.43E+01	1.50E+01
350	1.50E+03	1.16E+04	4.02E+03	1.60E+01	1.13E+01
355	8.00E+02	1.19E+04	3.92E+03	1.04E+01	7.52E+00
360	5.50E+02	1.22E+04	3.82E+03	7.35E+00	3.76E+00
365	4.00E+02	1.07E+04	3.72E+03	5.25E+00	1.00E-03
370	2.00E+02	1.13E+04	3.63E+03	1.00E-03	1.00E-03
375	2.00E+02	1.03E+04	3.53E+03	1.00E-03	1.00E-03
380	2.00E+02	1.07E+04	3.43E+03	1.00E-03	1.00E-03
385	2.00E+02	1.00E+04	3.33E+03	1.00E-03	1.00E-03
390	2.00E+02	9.74E+03	3.23E+03	1.00E-03	1.00E-03
395	2.00E+02	9.44E+03	3.14E+03	1.00E-03	1.00E-03
400	2.00E+02	9.13E+03	3.04E+03	1.00E-03	1.00E-03

^a Molar absorptivity values were obtained from Behera et al. 2012.^b Molar absorptivity values were obtained from Yamamoto et al. 2009.^c Molar absorptivity values were obtained from Packer et al. 2003.^d Molar absorptivity values were obtained from Lin and Reinhard 2005.^e Molar absorptivity values were obtained from Kibbey et al. 2009.^f Molar absorptivity values were obtained from Ren et al. 2016.^g Molar absorptivity values were obtained from Tsai et al. 1992.^h Molar absorptivity values were obtained from Werner et al. 2005.ⁱ Molar absorptivity values were obtained from Chen et al. 2006.^j Molar absorptivity values were obtained from Latch et al. 2003a.^k Molar absorptivity values were obtained from Batchu et al. 2014.^l Molar absorptivity values were obtained from Talrose et al. 2016.

Table A1-6. Summary of predicted biodegradability of 55 TORCs generated by seven different BioWin versions.

TORCs	BionWin1	BionWin2	BionWin3	BionWin4	BionWin5	BionWin6	BionWin7
1,4-DCB	0.3127	0.0427	2.4611	3.3050	0.3200	0.1576	-0.3502
2,4-D	0.4821	0.2193	2.6040	3.6608	0.5174	0.2599	0.1360
Acetaminophen	1.0015	0.9886	2.8673	3.8748	0.4866	0.5090	-0.1124
Anthracene	0.9819	0.9995	2.2194	3.2478	0.2641	0.1949	-0.3817
Atrazine	0.0045	0.0000	2.0002	3.0969	-0.1219	0.0000	-0.5787
Benzo(a)pyrene	-0.0299	0.0000	1.8422	2.7815	0.0601	0.0350	-0.3091
Benzophenone	0.9238	0.9725	2.8180	3.5724	0.3699	0.3318	-0.0737
Bezafibrate	0.6784	0.5724	2.1583	3.6065	0.2728	0.0434	-1.1219
Bisphenol A	0.6866	0.4653	2.5953	3.4443	0.2956	0.1559	-0.2593
Bromoxynil	0.8178	0.7813	2.2892	3.1157	0.3742	0.1822	0.7259
Caffeine	0.6551	0.5625	2.7700	3.5676	0.1439	0.0521	0.5019
Carbamazepine	0.6351	0.4143	2.6770	3.5068	0.0873	0.0364	-0.0744
Carbofuran	0.7244	0.8785	2.3184	3.5773	0.2435	0.1936	0.0331
Chlorpyrifos	0.1928	1.0000	1.7442	3.2925	-0.0832	0.0014	0.5947
Ciprofloxacin	-0.3974	0.0000	1.9170	3.2138	0.0597	0.0001	-2.2865
Clofibric acid	0.4836	0.2918	2.6126	3.6820	0.5574	0.3741	-0.0765
DEET	0.9213	0.9724	2.6474	3.7087	0.4437	0.3954	-0.5924
Diazinon	1.0259	1.0000	2.5306	3.7369	0.1018	0.0292	0.5482
Diclofenac	0.1353	0.0027	2.2863	3.2984	-0.1313	0.0029	-0.8493
Diphenhydramine	0.3295	0.0647	2.4154	3.1914	0.0412	0.0313	-1.0880
Diuron	0.2717	0.0130	2.2709	3.1808	0.0565	0.0142	-0.4139
Doxycycline	-0.1442	0.0003	1.9339	2.9926	0.0326	0.0135	-1.0166
E ₁	0.6669	0.2801	2.2738	3.1846	0.2405	0.1074	-0.8995
E ₂	0.8178	0.6452	2.4518	3.3334	0.2903	0.1058	-0.3354
E ₃	0.9689	0.8159	2.5764	3.4398	0.3966	0.1237	-0.0432
EE ₂	0.4637	0.0702	2.0266	3.0158	0.1129	0.0354	-0.8418

Table A1-6. (Continued).

TOrcs	BionWin1	BionWin2	BionWin3	BionWin4	BionWin5	BionWin6	BionWin7
Fluoranthene	-0.0060	0.0000	1.9529	2.8537	0.1926	0.1079	-0.1182
Gemfibrozil	0.7584	0.8552	2.5906	3.6587	0.6680	0.6123	-0.2444
Ibuprofen	0.8314	0.8672	2.9582	3.7986	0.1976	0.1521	0.0334
Indomethacin	0.7087	0.4895	2.3587	3.4918	0.0740	0.0107	-0.4425
Iopromide	-0.9869	0.0000	1.7847	3.4495	-1.6210	0.0000	-0.9546
Ketoprofen	0.8888	0.8770	2.9265	3.7806	0.3192	0.1848	-0.1707
Linuron	0.2641	0.0104	2.2355	3.1577	0.0089	0.0090	-0.4139
MCPA	0.7289	0.8338	2.7809	3.7871	0.6134	0.5173	0.1665
Mefenamic acid	0.6851	0.7776	2.4692	3.2619	0.3540	0.1460	-0.5877
Metolachlor	0.4732	0.0789	2.1862	3.3963	0.0568	0.0153	-1.1361
Metoprolol	0.7720	0.6976	2.6511	3.6336	0.3331	0.1475	0.0709
Naproxen	0.8972	0.9611	2.9219	3.9097	0.4439	0.3447	0.3878
Nonylphenol	0.9215	0.9612	2.9921	3.7700	0.4443	0.5086	0.1979
Norfloxacin	-0.3916	0.0000	1.9435	3.2311	0.0934	0.0001	-2.1395
Octylphenol	0.9282	0.9680	3.0231	3.7903	0.4366	0.5025	0.1719
Phenanthrene	0.9819	0.9995	2.2194	3.2478	0.2641	0.1949	-0.3817
Phenol	0.9466	0.9876	3.0696	3.7565	0.5375	0.7105	0.6578
Progesterone	0.2436	0.0030	2.0350	3.0427	0.3623	0.0674	-1.7307
Propachlor	0.8736	0.9334	2.5260	3.6520	0.2507	0.0855	-0.3044
Pyrene	-0.0060	0.0000	1.9529	2.8537	0.1926	0.1079	-0.1182
Ranitidine	0.7003	0.1886	2.2985	3.1927	-0.2302	0.0009	-0.3500
Roxithromycin	-2.1892	0.0000	1.0176	2.4409	-0.3734	0.0000	-3.2504
Simazine	0.0112	0.0000	2.0312	3.1172	0.0195	0.0000	-0.3072
Sulfamerazine	0.4426	0.1116	2.4053	3.2895	-0.1411	0.0050	-0.3861
Sulfamethoxazole	0.4479	0.1281	2.4297	3.3054	-0.1165	0.0060	-0.2907
Testosterone	0.4079	0.0205	2.2750	3.2319	0.4828	0.1514	-1.1265

Table A1-6. (Continued).

TOrCs	BionWin1	BionWin2	BionWin3	BionWin4	BionWin5	BionWin6	BionWin7
Tetracycline	0.6199	0.0173	1.8151	3.0712	0.2719	0.0065	-2.4393
Triclosan	0.3102	0.0181	1.9378	3.0508	0.1780	0.0187	-0.6846
Trimethoprim	0.5922	0.9164	2.0385	3.3749	0.0889	0.0172	0.1677

Table A1-7. Summary of Freundlich isotherm information and Log K_{ow} for the 10 TOrCs used for testing correlation between adsorption performance and Log K_{ow}.

TOrCs	K (mg/g)(L/mg) ^{1/n}	1/n	Adsorbent Type	Adsorbent Details	log K _{ow}	pH	Ref.
1,1-Dichloroethane	1.79	0.53	Activated carbon	Calgon F300	1.79 ^a	5.30	U.S. EPA 1980
1,2-Dichloroethane	3.57	0.83	Activated carbon	Calgon F300	1.48 ^a	5.30	U.S. EPA 1980
1,2-Dichloropropane	5.86	0.60	Activated carbon	Calgon F300	1.98 ^b	5.30	U.S. EPA 1980
Acenaphthene	190	0.36	Activated carbon	Calgon F300	3.92 ^c	5.30	U.S. EPA 1980
Acenaphthylene	115	0.37	Activated carbon	Calgon F300	3.94 ^d	5.30	U.S. EPA 1980
Acetophenone	74.0	0.44	Activated carbon	Calgon F300	1.58 ^a	5.30	U.S. EPA 1980
Benzene	1.00	1.60	Activated carbon	Calgon F300	2.13 ^a	5.30	U.S. EPA 1980
Carbon Tetrachloride	11.1	0.83	Activated carbon	Calgon F300	2.83 ^a	5.30	U.S. EPA 1980
Chloroethane	0.59	0.95	Activated carbon	Calgon F300	1.43 ^a	5.30	U.S. EPA 1980
Chloroform	2.60	0.73	Activated carbon	Calgon F300	1.97 ^a	5.30	U.S. EPA 1980

^a Log K_{ow} values were obtained from Hansch et al. 1995.

^b Log K_{ow} value was obtained from Sangster 1994.

^c Log K_{ow} value was obtained from Hansch and Leo 1987.

^d Log K_{ow} value was obtained from Walters and Luthy 1984.

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APPENDIX B: Fate of Trace Organics in a Wastewater Effluent Dependent Stream

This article was published in Science of The Total Environment (2015)

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Abstract

Trace organic compounds (TOrcs) in municipal wastewater effluents that are discharged to streams are of potential concern to ecosystem and human health. This study examined the fate of a suite of TOrcs and estrogenic activity in water and sediments in an effluent-dependent stream in Tucson, Arizona. Sampling campaigns were performed during 2011 to 2013 along the Lower Santa Cruz River, where TOrcs and estrogenic activity were measured in aqueous (surface) and solid (riverbed sediment) phases. Some TOrcs, including contributors to estrogenic activity, were rapidly attenuated with distance of travel in the river. Those TOrcs that are not sufficiently attenuated and percolate to ground water have in common low biodegradation probabilities and low octanol–water distribution ratios. Independent experiments showed that attenuation of estrogenic compounds may be due in part to indirect photolysis caused by formation of organic radicals from sunlight absorption. Hydrophobic TOrcs may accumulate in riverbed sediments during dry weather periods, but riverbed sediment quality is periodically affected through storm-related scouring during periods of heavy rainfall and runoff. Taken together, evidence suggests that natural processes can attenuate at least some TOrcs, reducing potential impacts to ecosystem and human health.

Keywords: trace organic compounds; estrogenic activity; solar photolysis; effluent dependent stream.

B.1 Introduction

For more than thirty years, it has been known that pharmaceuticals, personal care products and other trace organic contaminants (TOrcs) survive conventional wastewater treatment and persist in the environment to varying degrees (Richardson and Bowron 1985; Ahel et al. 1994a; Kolpin et al. 2002). More than any other group of trace organics in municipal wastewater, endocrine disrupting compounds (EDCs) have attracted the attention of health professionals and the public (Heberer 2002; Teske and Arnold 2008; Sumpter and Jobling 2013). These compounds interfere with normal endocrine function by blocking signaling/response (antagonists) or stimulating inappropriate activity (agonists). Chemicals present in municipal wastewater that promote estrogenic response include natural steroidal estrogens such as estrone (E_1), 17β -estradiol (E_2) and estriol (E_3), and anthropogenic mimics such as 17α -ethinylestradiol (EE_2) and alkylphenols (APs) (Routledge and Sumpter 1996; Teske and Arnold 2008). All these compounds share similar chemical structure: presence of phenolic rings, similar molecular weight, and significant hydrophobicity ($\log D_{ow} > 3$). Early evidence of endocrine disrupting activity in treated wastewater arose from elevated incidence of intersex characteristics (compromised gonadal growth, spermatogenesis, sperm motility, and fertilization success) among male fish in rivers of the United Kingdom (Purdom et al. 1994; Jobling et al. 1998). E_2 and EE_2 elicit physiological changes in continuously exposed organisms at levels that are routinely measured in conventionally treated municipal wastewater effluent (Sanchez et al. 2011). Factors that influence the removal of EDCs and other TOrcs during wastewater treatment have been widely studied. Simulations of conventional treatment have not, however, been entirely successful in predicting

chemical-specific removal efficiencies during municipal wastewater treatment (Rojas et al. 2010).

Gross et al. (2004) studied the fates of TOrCs in an effluent dominated stream and wetland in southern California, measuring attenuations of ibuprofen, gemfibrozil and chlorinated tris-propylphosphates as well as the conversion of alkylphenol polyethoxylates to APs. Fono et al. (2006) measured the attenuations of ethylenediaminetetraacetate (EDTA), gemfibrozil, ibuprofen, metoprolol, naproxen, and total adsorbable organic iodide in the Trinity River, an effluent dominated stream in Texas. Although the iodated compounds were conserved, others decreased in concentration by 60–90% during two weeks of travel over 500 km. In a more recent Arizona survey, Chiu and Westerhoff (2010) found that surface water concentrations of sucralose, sulfamethoxazole, acetaminophen, cotinine, dilantin, caffeine, DEET and oxybenzone exhibited seasonal trends. Oxybenzone and sucralose concentrations were generally higher in summer months due to increased recreational use of surface water resources.

Candidate mechanisms for the attenuation of trace organics during in-stream transport include biodegradation, photolysis and adsorption on riverbed sediments (Barber et al. 2013; Hanamoto et al. 2013; Writer et al. 2013). Conditional rate constants representing relative compound biodegradability have been based on either direct measurement (Salveson et al. 2010) or moiety-specific contributions to biological transformation rates (ASTreat 1.0, a windows based computer model designed by Procter and Gamble Company, McAvoy, 1999). The contribution of sorption on organic solids should be directly related to compound hydrophobicity, as reflected by octanol/water partitioning

(K_{ow} or D_{ow}) (Ying et al. 2002; Snyder et al. 2003). It is expected that, other factors being equal, compound hydrophobicity would lead to accumulation in river sediments due to both sedimentation and the retention of contaminants during infiltration. Direct photolysis and indirect photolysis also contribute to in-stream compound disappearance (Watts and Linden 2008; Wols and Hofman-Caris 2012). Direct photolysis occurs when a compound undergoes transformation as a result of light absorption. This is envisioned as a two-step process in which the absorption of light energy promotes the compound to an excited state, after which either chemical transformation occurs or the excited compound devolves to its original ground state. Indirect photolysis is initiated through light absorption by other chemicals, leading to production of reactive intermediates such as hydroxyl or organic radicals that react chemically with the target compound (Wols and Hofman-Caris 2012). Jasper and Sedlak (2013) hypothesized that radicals formed by direct photolysis of dissolved organic matter could be responsible for indirect photolysis of TOrCs. Schwarzenbach et al. (2003) analyzed how radicals (hydroxyl, carbonate, organics, etc.) produced by direct photolysis of certain compounds may attack TOrCs and degrade them.

The Santa Cruz River (SCR) is an effluent dependent stream in Tucson, Arizona (Figure B-1). Except during widespread precipitation events, the only source of river water is the treated wastewater from two wastewater treatment facilities. The SCR is located in an inner valley created by dissected pediments and alluvial deposits. Consequently, the riverbed is made up of fine sand and gravel eroded from surrounding mountains. Prior to 2014, the Pima County Regional Wastewater Reclamation Department's (PCRWRD) two major wastewater treatment plants discharging to the SCR were the Roger Road

Wastewater Treatment Plant (RRWTP; trickling filter, treatment capacity of $1.80 \text{ m}^3/\text{s}$) and the Ina Road Water Reclamation Facility (IRWRF; activated sludge, treatment capacity $1.64 \text{ m}^3/\text{s}$). The plants are the main wastewater treatment facilities for the City of Tucson, with about half a million inhabitants. Due to a mandate by the State of Arizona requiring nutrient removal, in February 2014 the RRWTP was decommissioned and replaced by the Agua Nueva Water Reclamation Facility (WRF) and the IRWRF was similarly upgraded and renamed the Tres Rios WRF. This study was conducted prior to the new WRFs going online. Together, the two upgraded WRFs discharge $\sim 50,000$ AFY (acre-feet per year) ($1.96 \text{ m}^3/\text{s}$) of municipal wastewater effluent to the SCR. Galyean (1996) estimated that about 90% of the treated wastewater effluent discharged to the SCR infiltrates within a 25-mile (40 km) length downstream from the RRWTP. With the improved effluent quality discharged to the SCR since early 2014, it is anticipated that infiltration rates in the riverbed will increase, due to reduction of suspended solids concentration or decrease in microbial activity in the sediments, and the length of the wetted reach will decrease relative to the period prior to February 2014. In a 1999–2000 nationwide survey of the United States surface waters, the US Geological Survey measured some of the highest in-stream concentrations of trace organics at a sampling point in the lower SCR, several miles downstream from the IRWRF outfall (Kolpin et al. 2002). The rainfall pattern in southern Arizona typically includes brief periods of heavy precipitation in the summer months (the North American monsoon) that motivate equally brief periods of high stream flow (Figure B1-1). It has been shown that these events tend to scour sediments in the SCR, redistributing deposits that accumulate over the remainder of the year (Lacher 1996). It is expected that high flow conditions in the river will

produce discontinuities in time-dependent sediment concentrations of trace organic contaminants, although this has not been confirmed via direct measurement.

Figure B-1. Wastewater treatment facilities and sampling sites along the Santa Cruz River (blue line) in Tucson, AZ. Red dots: major water reclamation facilities; black stars: sampling sites in the 2011 campaign (river water and groundwater wells); green dots: river water sampling sites in the 2012–13 campaigns. Relative distances for all sampling points are reported in Tables B-4 and B-5. In February 2014, the Roger Road Wastewater Treatment Plant (RRWTP) was replaced by the Agua Nueva Water Reclamation Facility (WRF); and the Ina Road Water Reclamation Facility (IRWRF) was similarly upgraded and renamed Tres Rios WRF. Except during periods of widespread rain, the SCR only flows along the northwest direction from the RRWTP, and the tributaries seen in the figure are completely dry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In this work, concentrations of TOrCs of wastewater origin (measured via liquid and gas chromatography/mass spectrometry) and estrogenic activity (measured using the Yeast

Estrogen Screen assay) were determined in SCR surface waters, groundwater samples obtained from monitoring wells proximate to the SCR, and riverbed sediments. The monitoring program and supplementary controlled experiments using local effluent were designed to test hypotheses regarding mechanisms of in-stream attenuation, including direct photolysis and indirect photolysis of estrogenic activity and humic-like substances; the latter assessed by fluorescence spectrometry. The work is timely in light of process improvements recently completed at the Agua Nueva WRF and Tres Rios WRF and consequent improvements in both effluent and environmental quality. The data provide a baseline against which the effects of process improvements can be measured. Our hypotheses related to natural in-stream attenuation mechanisms follow:

1. Biodegradable TOrCs, including those that contribute to estrogenic activity, are rapidly attenuated with distance of travel in the SCR. It is noted that dilution is not a candidate mechanism for contaminant attenuation, since the SCR is effluent dependent except during infrequent periods of rainfall/runoff.
2. Indirect or direct photolysis may be a predominant mechanism in the attenuation of some TOrCs, including estrogenic compounds.
3. Riverbed sediments are a potential sink for TOrCs during dry weather periods due to sorption and/or biodegradation. Scouring of sediments during storm periods plays a role in the redistribution of TOrCs along the river.

B.2 Materials and Methods

B.2.1 Chemicals and Reagents

All TOxCs measured in this work (Table B-1) were reagent grade or better and used as obtained. Bisphenol A and tris (2-chloroethyl) phosphate (TCEP) were from TCI America (Portland, OR). N,N-diethyl-metatoluamide (DEET), ibuprofen, triclosan and perfluorooctanesulfonic acid (PFOS) were from Alfa Aesar (Lancashire, UK). Iopromide was from USP (Rockville, MD). Tonalide was purchased from Toronto Research Chemicals (Toronto, Canada). Sucralose was from AK Scientific (Union City, CA). Perfluorohexadecanoic acid (PFHxDA) was from Matrix Scientific (Columbia, SC) and meprobamate was from Cerilliant (Round Rock, TX). The rest of the compounds were acquired from Sigma-Aldrich (St. Louis, MO). Compounds were selected based on their presence in conventionally treated wastewater effluent in previous studies and the existence of sufficiently sensitive analytical methods. Together, they provide a broad range of physical/biochemical characteristics, allowing us to investigate hypothesized cause–effect relationships governing contaminant fates in surface waters.

Isotopically labeled internal standards were from three sources. $^{13}\text{C}_4$ -PFOA, $^{13}\text{C}_4$ -PFOS, $^{13}\text{C}_2$ -PFHxDA, and $^{13}\text{C}_4$ -PFBA were from Wellington Laboratories (Ontario, Canada). $^{13}\text{C}_6$ -diclofenac, primidone- d_5 , ibuprofen- d_3 , sulfamethoxazole- d_4 , triclosan- d_3 and iopromide- d_3 were from Toronto Research Chemicals (Toronto, Canada). Gemfibrozil- d_6 , 4-nonylphenol- d_4 , estrone- d_4 , DEET- d_7 , carbamazepine- d_{10} and bisphenol A- d_{16} were from C/D/N Isotopes (Quebec, Canada).

Table B-1. Relevant physical/chemical properties for TOrCs measured in the Santa Cruz River water during the sampling campaigns in 2011 (in boldface) and in riverbed sediments. EE₂ was not measured directly, but used as a reference for quantification of estrogenic activity.

Compound	Usage	Log Dow at pH=7 ^a	k _{OH} (10 ⁹ M ⁻¹ s ⁻¹)	P _B ^b	Log K _{AW} ^c	Monitoring event ^d
17 α -Ethinylestradiol (EE ₂)	Estrogen	4.11	10.3 $\pm$ 0.7 ^e	0.0354	-9.489	
4-nonylphenol	Derived from detergents	6.14	11.0 $\pm$ 0.2 ^f	0.5086	-2.857	LS
4-octylphenol	Derived from detergents	5.63	14.0 $\pm$ 0.2 ^f	0.5025	-3.735	LS
Atenolol	b-blocker	-2.09	7.10 ^g	0.2349	-16.252	S
Atrazine	Herbicide	2.64	2.30 $\pm$ 0.14 ^e	0	-7.016	S
Benzophenone	Photo initiator	3.21	NA	-0.0737	-4.101	S
Benzotriazole	Drug precursor	1.42	NA	0.3935	-5.221	S
Bisphenol A	Plasticizer	3.64	8.00 $\pm$ 3.11 ^e	0.1559	-9.427	S
Carbamazepine	Anticonvulsant	1.89	8.02 $\pm$ 1.90 ^e	0.0364	-8.355	LWS
Caffeine	Stimulant	-0.63	6.40 $\pm$ 0.71 ^e	0.0521	-8.835	S
DEET	Insect repellent	2.42	5 ^g	0.4437	-6.07	LWS
Dexamethasone	Anti-inflammatory and immunosuppressant	2.03	NA	0.0015	-5.534	LWS
Diclofenac	Nonsteroidal anti- inflammatory drug (NSAID)	1.77	8.38 $\pm$ 1.24 ^e	0.0029	-9.714	S
Diltiazem	Calcium channel blockers	2.98	NA	0.0267	-14.453	S
Diphenhydramine	Antihistamine	1.25	5.42 ^e	0.0313	-6.82	S
Fluoxetine	Anti-depressant	1.15	9.60 $\pm$ 0.80 ^h	0	-5.439	LWS
Gemfibrozil	Blood lipid regulator	2.07	10.0 $\pm$ 0.60 ⁱ	0.6123	-6.313	S
Ibuprofen	Nonsteroidal anti- inflammatory drug (NSAID)	0.94	7.04 $\pm$ 0.52 ^e	0.1521	-5.207	S
Meprobamate	Anxiolytic	0.7	NA	0.314	-8.121	S
Naproxen	Nonsteroidal anti- inflammatory drug (NSAID)	0.73	8.61 ^e	0.3447	-7.858	S
Norgestrel	Hormonal contraceptives	3.37	NA	0.0469	-7.502	S
PFBS	Surfactant	-1.81	NA	0	-3.23	S

Table B-1. (Continued).

Compound	Usage	Log Dow at pH=7 ^a	k _{OH} (10 ⁹ M ⁻¹ s ⁻¹)	P _B ^b	Log K _{AW} ^c	Monitoring event ^d
PFDA	Surfactant	4.15	NA	0	2.011	S
PFDoA	Surfactant	5.61	NA	0	3.452	S
PFOA	Surfactant	2.69	0.01 ^j	0	0.57	LWS
PFOS	Surfactant	1.01	0.01 ^j	0	-0.347	LWS
PFHxDA	Surfactant	8.53	NA	0	6.334	S
Prednisone	Immunosuppressant	1.57	NA	0.1452	-7.937	S
Primidone	Anticonvulsant	0.83	6.70 ^e	0.4211	-8.101	LWS
Propylparaben	Preservative	2.88	NA	0.8344	-6.584	S
Simazine	Herbicide	2.28	2.90 ± 0.28 ^e	0	-7.414	S
Sucralose	Artificial sweetener	0.23	1.50 ± 0.10 ^k	0.004	-16.787	LWS
Sulfamethoxazole	Antibiotic	-0.22	5.82 ± 1.99 ^e	0.006	-10.408	LWS
Testosterone	Steroid hormone	3.18	NA	0.1514	-6.841	S
Triclocarban	Antibiotic	6.07	NA	0.0017	-8.733	S
Triclosan	Antibiotic	5.28	5.40 ^l	0.0187	-6.69	S
Trimethoprim	Antibiotic	0.27	6.30 ± 0.85 ^e	0.0172	-12.01	LWS
TCEP	Flame retardant	-5.91	2.00 ^m	0.0193	-3.871	LWS
TCPP	Flame retardant	2.53	27.1 ^m	0.0013	-5.613	S
Tonalide	Aromatic musk	5.06	4.72 ⁿ	0.0737	-2.245	LW
Iopromide	Contrast medium	-2.66	3.30 ^e	0	-26.388	LW

Note: Log D_{OW}: n-octanol–water distribution ratio at pH 7; k_{OH}: second-order reaction rate constant between compound and hydroxyl radical; P_B: probability of biodegradation; K_{AW}: air–water partition coefficient.

^a Data directly obtained from SciFinder.

^b Calculated by Biowin6 (MITI Non-Linear Model). US EPA; Estimation Program Interface (EPI) Suite. Ver. 4.1.

^c Calculated by KOAWIN. US EPA; Estimation Program Interface (EPI) Suite. Ver. 4.1.

^d Monitoring event: indicates sampling events in which the compound was measured: W—monitoring well, L—river liquid, S—sediment. For example, for NP, LS means that it was measured in liquid and sediment but not in well sampling.

^e As reported by Wols and Hofman-Caris (2012).

^f As reported by Ning et al. (2007).

- ^g As reported by Song et al. (2008).
^h As reported by Lam et al. (2005).
ⁱ As reported by Razavi et al. (2009).
^j As reported by Hyunwoong (2010).
^k As reported by Toth et al. (2012).
^l As reported by Dodd et al. (2009).
^m As reported by Machairas (2004).
ⁿ As reported by Ward (2010).

Stock solutions of target analytes and internal standards were prepared in 50 v% water/methanol. Calibration and fortification solutions were prepared by successive dilution of stocks to 10 µg/L in methanol. Liquid chromatography solvents were of the highest purity available. Methanol, acetonitrile and formic acid were purchased from EMD Chemicals (Gibbstown, NJ). Methyl tert-butyl ether (MTBE) and ammonium hydroxide were from Fisher Scientific (Pittsburgh, PA). LCMS reagent water was obtained from J.T. Baker (Center Valley, PA).

B.2.2 Sample Collection and Preparation

Sample collection vessels and all glassware were cleaned with methanol and rinsed three times with ultrapure water, then heated in Thermolyne 6000 Muffle Furnace (Dubuque, IA) at 550 °C for 5 h prior to use. In spring and summer 2011, sampling was performed three times at the RRWTP outfall and at twelve locations along the 37-km reach for surface and ground water (Figure B-1). The groundwater samples near the river were obtained from a series of twelve monitoring wells owned by the PCRWRD. The relative contribution of river water and ground water to well samples was assessed in a previous work (Quanrud et al. 2004). Collection of samples was done during dry periods, i.e. absence of precipitation.

Liquid samples were filtered through 0.7 µm glass fiber filters (Pall Corporation, Fort Washington, NY) before deuterated internal standards were added. Samples were then extracted using Oasis HLB SPE cartridges (Waters, Milford, MA). HLB sorbents were first conditioned by stepwise addition of 5 mL of methanol, 5 mL of MTBE and 5 mL of water. A half gram of EDTA was dissolved in 1 L of each water sample before it was

loaded onto the SPE sorbent at 10 mL/min using a Dionex™ AutoTrace™ 280 Solid-Phase Extraction (SPE) instrument (Thermo Scientific, Pittsburgh, PA). Following the sorption step, sorbents/ adsorbates were dried under nitrogen gas for 40 min before they were sequentially eluted with 3 mL of methanol, 3 mL of 5% NH₄OH in MeOH, 3 mL of acetonitrile and 3 mL of MTBE. The combined eluents were evaporated to about 50 µL and re-dissolved in 1mL of 50% water/methanol for liquid chromatography tandem mass spectrometric (LC/MS) analysis.

In 2012–2013, sampling was performed four times at the RRWTP outfall and at five downstream locations along the same study reach for surface water and riverbed sediments (Figure B-1). Locations were chosen based on ease of access, position in the river (0–37 km extending northwest from the RRWTP outfall) and presence of representative riverbed sediments. The river was dry upstream of the RRWTP outfall, except during storm runoff episodes. At each sampling point, 4-L grab samples of surface water were collected. The monitoring program was designed to provide samples before (June 22, 2012), during (July 18, 2012) and after (October 13, 2012) the summer precipitation period (July–September—North American monsoon). A fourth set of samples was collected after a winter rainfall event (February 3, 2013). At each sampling site/time, one riverbed surface sediment sample and one sediment core sample (5 cm in diameter) were collected. These were subsequently used to produce sediment samples, hereinafter referred to as surface sediment (0–2.5 cm) and bottom core sediment (10.2–12.7 cm). Surface sediment samples were obtained using a clean stainless steel trowel. Core samples were collected using a purpose-built stainless steel core sampler (Rickly Hydrological Co., Columbus, OH; model 603–004) that was driven into the riverbed and

then withdrawn. Cores were retained in the sampler during withdrawal by a core catcher mechanism. Sediment cores and samples were transferred to muffled glass jars, stored at 4 °C and extracted on the day after collection.

Each sampling campaign (surface water and sediments) consisted of a one-day sampling event. Sampling started at the furthest downstream point (N. Trico Rd., Figure B-1) at approximately 10 am and finished at the RRWTP effluent site at approximately 5 pm. The possibility of diurnal variability of TOxC concentrations was not explored in the present work.

Two liters of each surface water sample was filtered through a 0.7 µm Whatman GF/F glass fiber filter (GE Healthcare). The pre-weighed filters and non-filterable solids were dried for 48 h at 60 °C and reweighed to establish suspended solids concentrations before organics in the suspended solid of river samples were extracted via microwave-assisted extraction (MAE) using a Microwave Accelerated Reaction System (MARS, CEM Corporation, Glendale, CA) (Lopez-Avila et al. 1994; Eskilsson and Björklund 2000; Sanchez-Prado et al. 2010). For suspended solids, the whole dried portion retained on the glass fiber filter was used. For riverbed sediment extractions, about 3 g of dried sediment was used. The samples were conditioned overnight in 15 mL methanol in Teflon microwave vessels ahead of MAE extractions (70 °C for 60 min). Extracts were poured off and saved, after which vessels and residual sediments were rinsed twice with 5 mL methanol. The pooled extracts were then dried under a gentle stream of N₂ gas before residual organics were re-dissolved in 1 mL methanol. In order to clean the extracts, the methanol containing extracted organics was diluted to 250 mL with nanopure water before the mixture was slowly passed under vacuum through 47 mm Empore™

Extraction Disks (octadecylsilane, 3M, Eagan, Minnesota). Retained organics were separated by sequential elution in a stepwise methanol gradient using 15 mL washes consisting of 20%, 50%, 80% and 100% (v/v) methanol in water. Half of each eluent mixture was added to a single 40-mL glass vial and stored at 4 °C for further processing. The other half was dried under nitrogen and redissolved in nanopure water for analysis of estrogenic activity. To eliminate bacterial contamination, samples for measurement of estrogenic activity were autoclaved at 121 °C for 10 min prior to analysis (Littlehat 2007). For cases in which analytical measurements could not be performed within 24 h of sample collection, samples were hermetically sealed and stored at 4 °C.

B.2.3 Yeast Estrogen Screen (YES) Bioassay Method

The YES bioassay, based on that of Routledge and Sumpter (1996), was used to measure estrogenic activity in sample extracts. The test organism was a recombinant strain of *Saccharomyces cerevisiae* in which the DNA sequence of the human estrogen receptor (hER- α) was integrated into the yeast genome. The yeast strain also contains expression plasmids carrying estrogen-responsive sequences (EREs) controlling transcription of the reporter gene *lacZ* (encoding β -galactosidase). In the presence of estrogen, β -galactosidase is synthesized in the cells. Its activity is measured colorimetrically. Sample extracts were serially diluted across 96-well micro-titer plates (Corning Costar®, Corning, NY). In positive controls, refreshed cells were added to serial dilutions of standard hormone (EE₂) preparations. Cell suspensions were incubated for 24 h at 32 °C in the presence of either the prepared extracts or known concentrations of EE₂ for growth and hormone-dependent gene expression. After that, 50 μ L of cycloheximide (4 mg/mL)/CPRG (chlorophenol red β -D-galactopyranoside, 0.4 mg/mL) solution was

added to each test well. Following an additional incubation for 24 h at 32 °C, color was measured: $A_{570} - R \times A_{630}$, using a UV–VIS microplate reader (Bio-tek Instruments, Winooski, VT), where A is absorbance at the indicated wavelength (nm), and R is the ratio of optical densities at 570 nm and 630 nm in negative controls. Color was converted to total sample estrogenic activity using results of the contemporary positive control. To compare standards and samples from one event to another, data were normalized as follows:

$$\% \text{relative estrogenic activity} = \frac{A_{\text{sample}} - A_{\text{background}}}{A_{\text{maximum}} - A_{\text{background}}} \times 100\%$$

In the equation, A_{maximum} and $A_{\text{background}}$ are the maximum and the negative control absorbances at 570 nm for the standard curve (EE₂ solution), and A_{sample} is the absorbance of the sample. The percent relative estrogenic activity for the sample was the estrogenic activity indicated relative to the standard curve run along with the data set. That is, the range of response observed in the standard was used to normalize the data from the sample.

A practical quantification limit (PQL) for the assays was arbitrarily adopted as the EC₂₀ value for EE₂ divided by the highest sample concentration factor tested in the YES procedure (normally 400). Below the PQL was a method detection limit (MDL). The MDL was the EE₂ concentration that produced a test response equal to 3 times the standard deviation in ($A_{570} - R \times A_{630}$) in hormone-free (blank) test wells, divided by the highest concentration factor tested.

B.2.4 Gas Chromatography–Mass Spectroscopy

An Agilent 6890 gas chromatograph and Agilent 5973 mass-selective detector were used for GC–MS analyses of nonylphenol (NP) and octylphenol (OP). Compounds were separated on a fused silica column (HP5-MS, 30 m $\times$ 0.25 mm i.d., 0.25 μ m film thickness, Agilent, Santa Clara, CA). The oven temperature program used was: 1 min at 90 $^{\circ}$ C, ramp at 15 $^{\circ}$ C min $^{-1}$ to 220 $^{\circ}$ C, hold for 2 min, ramp at 15 $^{\circ}$ C min $^{-1}$ to 240 $^{\circ}$ C, followed by 10 $^{\circ}$ C min $^{-1}$ to 280 $^{\circ}$ C. Helium was the carrier gas at a constant flow rate of 1 mL min $^{-1}$. The inlet, transfer line and ion source were at 250, 280 and 230 $^{\circ}$ C, respectively. Sample injection (1 μ L) was in splitless mode. The mass detector was operated in the electron ionization mode using the selected ion monitoring (SIM) method. Quantification ions were as follows: m/z 135 for NP and m/z 107 for OP. The limit of detection (LOD) and limit of quantification (LOQ) were defined as three times and ten times the signal-to-noise ratio (Komori et al. 2004).

B.2.5 Liquid Chromatography–Mass Spectrometry

An Agilent 1290 Infinity LC System and Agilent 6460 Triple Quadrupole LC/MS system with both positive and negative electrospray ionization were used for analyses of other trace organic contaminants. Multiple-reaction monitoring mode was used for fragmentation data, monitoring both quantifiers (highest response product ion) and qualifiers (next highest product ion) for each compound measured. Calibration curves contained at least five points, with $R^2 > 0.99$ for linear fits. LOD and LOQ were defined the same as in the GC–MS analytical work. When surrogate (isotope) recovery was less

than 5%, concentrations were flagged as non-detectable due to disappearance during extraction.

B.2.6 Photodegradation of Estrogenic Activity in Secondary Effluent

Milli-Q water (18 M Ω) was prepared using a Millipore water purification system (Billerica, MA). Secondary effluent from the RRWTP was spiked with EE₂ (0.32 nM). Irradiation experiments were done in direct sunlight in cloud-free weather. Five glass photoreactors, containing 600mLMilli-Q water or secondary effluent plus EE₂ were set up in parallel and sacrificed at 0, 0.5, 1, 2 and 4 h for analysis via excitation– emission matrix (EEM) fluorescence spectroscopy and the YES bioassay (estrogenic activity). Dark controls were set up and sacrificed after 4 h for the same set of measurements.

Fluorescence of secondary effluent samples was characterized by a PerkinElmer LS 55 fluorescence spectrophotometer (Waltham, MA). The inner filter effect (IFE) caused by light absorption and reabsorption of emitted light by light-absorbing compounds was corrected by a mathematical model that takes into account the absorption spectrum of the sample (MacDonald et al. 1997). A Thermo Scientific Genesys 10S UV–Vis spectrophotometer was employed to obtain the absorption spectra of test samples. EEM fluorescence data obtained from the fluorescence spectrophotometer corresponded to scan ranges of emission and excitation wavelengths of 280 to 400 nm. Scan speed was 600 nm/min.

To investigate the role of photolysis in attenuating estrogenic activity in the SCR, batch reactors containing either wastewater effluent from the RRWTP or Milli-Q water were spiked with 0.32 nM EE₂ and exposed to sunlight on the University of Arizona campus

for a period of 4 h (10 am to 2 pm) on cloudless days. A dark control was maintained over the same period, and a second control consisted of wastewater effluent without supplementary EE₂. Samples were withdrawn for separation and measurement of liquid phase estrogenic activity at the start of the experiment and after 0.5, 1.0, 2.0 and 4.0 h of exposure. In addition, fluorescence excitation–emission matrix (EEM) measurements were carried out on each sample. Preliminary tests designed to measure recovery of estrogenic activity from wastewater effluent spiked with EE₂ showed that the extraction procedure recovered essentially all of the spiked EE₂ plus the contribution from estrogenic TOrCs originally present in the effluent.

B.3 Results and Discussion

B.3.1 Trace Organics Attenuation in the Santa Cruz River

A suite of twelve dissolved TOrCs (Table B-1) were measured over the same (37-km long) reach of the SCR during three sampling campaigns in 2011, while p-nonylphenol (NP) and p-octylphenol (OP) were measured separately during a February 2013 sampling event. It is important to point out that the only source of water to the SCR in the river reach analyzed in the absence of rain is the discharge from the wastewater treatment plants. That is, there are no flowing tributaries and no groundwater input to the river, as shown by Quanrud et al. (2004).

For the sampling campaigns in 2011, the twelve TOrCs measured were detected in the effluents of both the RRWTP and IRWRF and at all twelve sampling points along the 37-km study reach of the Santa Cruz River. Average concentrations and standard deviations for each compound from these three sampling periods are provided in Table B1-1. TOrCs

present at the highest concentrations were sucralose, sulfamethoxazole, trimethoprim and DEET. Of these compounds, DEET, trimethoprim, and iopromide were substantially higher in effluent from the RRWTP than in the IRWRF effluent, whereas the reverse was true for primidone and fluoxetine.

Since the IRWRF is located about 7.5 km downstream of the RRWTP, and the contribution of TOrCs from the IRWRF secondary effluent to the SCR may be significant, only the distributions of contaminant concentrations between the IRWRF and the end of our survey area (37 km downstream of the RRWTP) were representative of attenuation. Profiles of TOrC concentration with distance downstream from the IRWRF (Figure B-2a and b) indicate that tonalide, fluoxetine, iopromide, sucralose (not shown) and PFOS were attenuated during surface transport along the 37-km studied reach of the river. Carbamazepine, DEET, sulfamethoxazole, TCEP, trimethoprim and primidone were conserved. Musolff et al. (2009) reported attenuation of tonalide in surface waters while carbamazepine results were inconclusive. These trends are consistent with our findings.

Figure B-2. In-stream TOrC surface water concentration versus distance traversed in the Santa Cruz River downstream from the RRWTP. Solid lines are linear fits of the data downstream of the IRWRF. Regression data are shown in Table B-2: (a) tonalide and fluoxetine; (b) iopromide and PFOS; (c) p-nonylphenol and p-octylphenol. Values presented represent measurements from a single sampling campaign.

Concentrations of NP and OP in the SCR were measured during the February 2013 sampling event. In filtered river samples, NP concentrations ranged from 244–484 ng/L (Figure B-2c), which were smaller than the concentration of NP in the river at N. Cortaro Road (location in Figure B-1) reported by Kolpin et al. (2002). OP concentrations spanned the range of 8.6–101 ng/L, although only one stream sample was above 50 ng/L. This was within the range of results of Kolpin et al. (2002). Profiles of NP and OP concentration versus distance downstream followed the same trends, first decreasing below the RRWTP and then fluctuating modestly with distance in the stream reach immediately below the IRWRF outfall. The data are consistent with the hypothesis that are in-stream conversion of alkylphenol polyethoxylates and carboxylates (APnEOs and APnECs) to the more stable AP forms, as observed by others (Ahel et al. 1994b; Gross et al. 2004). Concentrations of NP were about 10-fold greater than OP in all river water samples, probably due to the widespread use of nonylphenol ethoxylates (NPnEOs) in industrial, agricultural, and domestic applications (Giger et al. 1984). Although in-stream loss was not observed here, previous work has shown that NP biodegrades under aerobic conditions during wastewater treatment and in receiving waters (Soares et al. 2008).

Attenuation and persistence trends in the position-dependent TOrC concentrations were examined using linear regression analysis. Examples are provided in Figure B-2, and results are summarized in Table B-2. The measured values decreased significantly with distance ($p \leq 0.05$) for five of the fourteen compounds (Table B-2). Candidate mechanisms for TOrC attenuation in the river include biodegradation, photolysis and sorption on bottom sediments or suspended solids. Since none of the TOrCs monitored was volatile (i.e., all had air–water partition coefficients $K_{AW} < 10^{-5}$, Table B-1), and

each survived conventional wastewater treatment, volatilization was neglected as a mechanism for in-stream attenuation.

Stepwise (backward) multiple linear regression was applied to analyze relationships between three independent variables ($\log D_{OW}$, P_B and k_{OH}) and attenuation of the trace organics in the river (dependent variable). Attenuation was represented by the normalized slope of compound concentration versus travel distance ($-B_0 / C_0$), where B_0 is the slope of the concentration vs. distance profile (Table B-2) and C_0 is concentration in the river sample just beyond the IRWRF outfall. Results (Table B-3) indicate that the three independent variables, alone or together, do not account for a significant fraction of the observed compound dependent attenuation in the Santa Cruz River, at least within the context of the linear model, and suggest that the responsible mechanism lies outside those proposed.

Table B-2. Results of least-square error linear regression analysis ($C = B_0x + B_1$, where C is surface water concentration and x is distance from the IRWRF outfall) in the Santa Cruz River liquid samples (for details see Supplementary information (APPENDIX B1)).

Compound	B_0 (ng/L km)	B_1 (ng/L)	R^2	P (significance)
Carbamazepine	0.610	280.8	0.077	0.437
DEET ^a	4.780	352.5	0.533	0.016
Sulfamethoxazole	7.629	879.6	0.175	0.229
TCEP	0.897	275.6	0.171	0.236
Tonalide ^a	-0.523	24.03	0.789	0.001
Fluoxetine ^a	-1.123	36.38	0.901	<0.0005
Trimethoprim	-1.961	184.1	0.248	0.143
Primidone	-0.194	179.6	0.011	0.777
Iopromide ^a	-1.001	70.30	0.451	0.033
Sucralose ^a	-94.15	6321	0.580	0.010
PFOS ^a	-1.145	41.84	0.468	0.029
PFOA	-0.123	11.88	0.062	0.448
4-n-Nonylphenol	-1.009	362.5	0.020	0.859
4-Octylphenol	0.532	18.17	0.244	0.506

^a Compound attenuation was statistically significant ($p \leq 0.05$).

Table B-3. Sequential multiple linear regression results (see text for explanation) for correlation between the normalized attenuation slope ($-B_0 / C_0$) in river surface water samples and the indicated compound properties. B represents the fitted coefficient of proportionality with respect to each listed independent variable. The standardized coefficients (β) represent the change (in number of standard deviations) of the dependent variable induced by a change of one standard deviation of the corresponding dependent variable (for details see Supplementary information (APPENDIX B1)).

Model		Correlation coefficients		Standardized coefficients	Significance (p)
		B	Std. error	β	
1	(Constant)	9.463	6.420		0.171
	Log D _{OW}	1.415	1.475	0.274	0.360
	P _B	-0.330	0.115	-0.844	0.017
	k _{OH} (M ⁻¹ s ⁻¹)	0.720	1.191	0.160	0.559
2	(Constant)	12.234	4.364		0.017
	Log D _{OW}	1.586	1.406	0.307	0.283
	P _B	-0.309	0.106	-0.791	0.014
3	(Constant)	12.401	4.411		0.016
	P _B	-0.242	0.089	-0.618	0.019

B.3.2 In-Stream Attenuation of Estrogenic Activity

Estrogenic activity was measured in the SCR during each of the four sampling campaigns (2012–2013) to indirectly establish probable attenuation mechanisms (Figure B-3a). Low estrogenic activities during the July and February sampling periods may reflect dilution due to storm waters, since the sampling was preceded by precipitation events (Figure B-1). The measured estrogenic activity in the RRWTP effluent (0 km point in Figure B-3a) was almost two orders of magnitude higher than levels that feminize continuously exposed fathead minnows (*Pimephales promelas*) (Länge et al. 2001). Just 1.50 km below the RRWTP outfall, estrogenic activity was ~20–25% of measured levels in the RRWTP effluent. Travel time from the RRWTP outfall to that point is estimated at 1 h. Despite the rapid attenuation of estrogenic activity, measured values exceeded concentrations necessary to disrupt sexual differentiation and reproduction in

continuously exposed organisms over a distance of ~10 km below the outfall. Total estrogenic activity in the SCR did not increase at the IRWRF outfall located about 7.7 km below the RRWTP (Figure B-3a). Beyond 11 km downstream from the RRWTP, estrogenic activity fell below the detection limit, estimated as 1.5×10^{-13} M (equivalent concentration of EE₂). Log D_{OW} values for estrogenic compounds in wastewater lie in the range of 3–6 (e.g. EE₂, OP and NP, Table B-1), suggesting that attenuation of their aqueous (river)-phase concentrations is due in part to sorptive partitioning on organic-rich solids (Lee and Liu 2002; Drewes et al. 2005). However, the contribution of estrogenic activity in extracts derived from instream suspended solids was <20% of total estrogenic activity in all SCR samples and usually much less (Figure B-3b), perhaps due to low residual suspended solids concentrations in plant effluents. Consequently, it is unlikely that sorption/sedimentation is a major contributor to loss of estrogenic activity with travel distance in the SCR.

As indicated previously, NP and OP concentrations in the river decreased much more slowly than total estrogenic activity. Furthermore, representative factors for converting NP and OP concentrations to equivalent concentrations of EE₂ are 7.0×10^{-5} and 3.3×10^{-6} , respectively (Routledge and Sumpter 1996). Thus, in samples taken close to the treatment plants, it is unlikely that NP and OP contributed significantly to total sample estrogenic activity (Table B-4).

Figure B-3. (a) Aqueous (river)-phase and (b) suspended solid estrogenic activity as a function of position in surface water from the Santa Cruz River. Dates shown are those of sample collection. Suspended solids were isolated from river water samples by filtering through 0.7 μm Whatman GF/F glass fiber filters.

Table B-4. Contributions of NP and OP to the total estrogenic activity in the liquid surface water samples. Calculations are based on the relative estrogenic activities of single estrogens in the YES test (Routledge and Sumpter, 1996), and an additive model for total estrogenic activity. See Figure B-1 for sampling locations.

Sampling point	Distance from RRWTP outfall (km)	Total estrogenic activity (M)	NP equivalent activity (M)	Percent NP for estrogenic activity	OP equivalent activity (M)	Percent OP for estrogenic activity
RRWTP effluent	0	7.51×10^{-11}	3.05×10^{-13}	0.41%	3.57×10^{-15}	0.048%
El Camino del Cerro	1.5	1.05×10^{-10}	2.21×10^{-13}	0.21%	5.08×10^{-16}	0.005%
N Silverbell Rd	7.2	2.67×10^{-12}	3.22×10^{-13}	12.1%	7.89×10^{-16}	0.296%
N Cortaro Rd	11.1	5.33×10^{-12}	2.82×10^{-13}	5.3%	3.03×10^{-16}	0.057%
Heritage Park Dr	26.9	1.33×10^{-11}	4.39×10^{-13}	3.3%	1.59×10^{-15}	0.120%
N Trico Rd	35.7	4.44×10^{-12}	2.23×10^{-13}	5.0%	8.75×10^{-16}	0.197%

B.3.3 Phototransformation Effects

Ground level spectral irradiance data during the solar irradiation experiments were obtained from SMARTS (Simple Model of the Atmospheric Radiative Transfer of Sunshine), a spectral irradiance simulation program that requires geographical information and atmospheric conditions for the experiment site and date (Gueymard 1995; Kaskaoutis and Kambezidis 2008). Atmospheric conditions were obtained from satellite data (OMI/Aura and MODIS) provided by Giovanni, a NASA database (Gueymard 2004). On the dates of the experiments (June 20, July 29 and August 13, 2013), the noontime ground level global spectral irradiances were indistinguishable (Figure B-4).

Figure B-4. Global spectral irradiance for the Tucson area for the dates of sunlight photolysis experiments.

In both the unspiked wastewater effluent control and the reactor containing effluent plus 0.32 nM EE₂, total estrogenic activity decreased below the method detection limit during the 4-hour period of solar light exposure (Figure B-5). Profiles of fractional removal versus time in spiked and unspiked effluent were similar: calculated half-lives for liquid phase estrogenic activity in the reactors were of the order of 1 h. Estrogenic activity did not change with time in dark controls and in Milli-Q water containing EE₂ that was exposed to sunlight (data not shown). The latter result shows that direct photolysis of estrogenic compounds is not an important mechanism for attenuation of estrogenic activity for the time scale explored in this work, including that encountered in the SCR. Jürgens et al. (2002) performed experiments on direct photolysis of E₂ and EE₂ under simulated sunlight in DI water and reported half times for the degradation of the estrogens of about 10 days. In 4 h (timescale of our experiments, Figure B-5), observed degradation of the targets was less than 3%, which is consistent with our results. The decrease in estrogenic activity in the spiked and unspiked effluent samples exposed to solar light suggests that indirect photolysis is the responsible mechanism for the attenuation of estrogenic activity with distance in the SCR. Indirect photolysis depends on the excitation of chromophores in the water sample. Subsequent dark reactions can produce a variety of organic radicals and hydrogen peroxide (e.g. Jasper and Sedlak 2013). Photolytic pathways leading to production of hydroxyl radicals can also begin with sunlight irradiance of aqueous-phase nitrate and nitrite ions and various iron complexes (Blough and Zepp 1995). A number of previous investigators have established the importance of dissolved organics in wastewater in similar photolytic reactions (Lin and Reinhard 2005; Leech et al. 2009; Hanamoto et al. 2013). The resistance of

estrogenic activity to attack via direct photolysis may be due to lack of light absorbance by the steroidal hormones at $\lambda > 310$ nm. Most energy in the solar spectrum is focused in the visible and infrared ranges ($\lambda > 380$ nm; Figure B-4) (Rosenfeldt and Linden 2004).

Figure B-5. Estrogenic activity changes in RRWTP secondary effluent during sunlight photolysis experiments. Results are shown for original samples and samples spiked with 0.32 nM EE₂.

The effect of effluent dissolved organic matter in sunlight-activated photolytic reactions is apparent in fluorescence EEM measurements (Figure B-6a). EEM peaks in the RRWTP effluent sample have been assigned to humic-acid-like (upper peak) and fulvic-acid-like (lower peak) substances (Chen et al. 2003). Attenuation of these peaks over the four-hour period of experimentation is apparent in the exposed reactors but not in the dark control (Figure B-6b). These results indicate that these fluorescent compounds are transformed during the 4-h period of exposure, making them candidate sources of organic

radicals for the indirect photolysis of TOrCs. Additional study is warranted to confirm the role of indirect photolysis as a fate mechanism.

(a)

(b)

Figure B-6. (a) Fluorescence excitation–emission matrix (EEM) test results for the RRWTP secondary effluent spiked with EE₂; color contour values represent light intensity (arbitrary units). (b) The humic (top) and fulvic (bottom) peaks of the EEM contours were attenuated after 4 h in sunlight but not in the dark (EE₂ does not contribute significantly to the high intensity regions in the EEM maps). I represents fluorescence intensity, obtained by integrating the EEM contours over a region of 5 nm around the maximum intensity point of the specified peaks; I_0 is the initial fluorescence intensity of the peak. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

B.3.4 Trace Organics in Monitoring Wells along the SCR

Twelve groundwater monitoring wells along the SCR (Figure B-1) were sampled during three campaigns in 2011. Eight of the twelve target TOxCs (compounds listed in Table B-2, excluding NP and OP) were detected in well water (Table B-5). The compounds not detected in the monitoring wells were DEET, TCEP, fluoxetine, and trimethoprim. There were substantial well-specific differences in TOxC concentrations, with the highest levels

generally in wells SC-3, SC-5, and SC-7. Quanrud et al. (2004) found that samples from SC-3 and SC-5 contained a substantially higher fraction of water derived from the infiltration of wastewater effluent than did other monitoring wells along the SCR. TOrC concentrations in the wells were generally at least an order of magnitude lower than respective river concentrations in SCR samples, and sulfamethoxazole and iopromide were about two orders of magnitude lower. Candidate mechanisms for compound attenuations include biodegradation, sorption and/or dilution with native groundwater. Exceptions included PFOS, PFOA, sucralose and carbamazepine, which were present at similar or higher concentrations in the wells than in river samples and suggested that dilution was not responsible when attenuation was observed. These four persistent TOrCs have in common relatively low biodegradation probabilities and low log D_{OW} values (Table B-1).

B.3.5 Trace Organics in Riverbed Sediments

TOrCs were measured in riverbed sediments during the February 2013 sampling event. Among the forty trace organic analytes (all the compounds in Table B-1 except EE₂), fourteen (Table B-6) were detected in sediment extracts. A number of those detected are hydrophobic and poorly biodegraded (Table B-1).

Carbamazepine was observed to persist in the liquid-phase in the SCR, consistent with studies done in other rivers (Tixier et al. 2003; Yamamoto et al. 2009). TCPP is structurally similar to TCEP, which was observed to persist in liquid phase samples in our study and elsewhere (Fries and Puttmann 2001; Yoon et al. 2010). The log D_{OW} of

TCPP indicates that it is hydrophobic as well, so this is not surprising to see it consistently appearing in the sediment samples along the SCR.

Table B-5. Concentrations of TOrCs (ng/L) in water samples from Santa Cruz River monitoring wells. See Figure B-1 for well locations.

Sampling point	Distance from RRWTP (km)	Depth of screened interval (m)	Carbamazepine	Sulfamethoxazole	Primidone	Iopromide
SC-1	0.8	33.5–45.7	191.2 ± 3.5	7.9 ± 0.1	134.4 ± 2.9	<MRL
SC-2	3.7	29.0–41.1	268.5 ± 55.3	15.2 ± 6.6	142.3 ± 10.4	1.4 ± 1.3
SC-3	8.4	27.4–39.6	369.1 ± 110.3	260.8 ± 81.1	184.9 ± 0.4	22.7 ± 4.1
SC-5	13.1	32.0–50.3	312.0 ± 96.4	55.0 ± 43.6	172.4 ± 33.5	2.0 ± 0.5
SC-6	14.8	35.1–56.4	374.5 ± 2.6	31.0 ± 1.5	227.8 ± 3.0	<MRL
SC-7	18.0	42.7–61.0	259.2 ± 57.2	62.1 ± 1.0	193.4 ± 4.0	1.4 ± 0.3
SC-8	20.0	61.0–91.4	202.4 ± 0.6	13.2 ± 2.3	59.5 ± 2.8	<MRL
SC-9	25.6	88.4–115.8	7.5 ± 0.4	9.0 ± 1.9	9.2 ± 0.1	<MRL
SC-10	27.2	91.4–112.8	12.3 ± 0.2	6.4 ± 0.1	12.4 ± 0.9	<MRL
SC-11	32.7	57.6–100.3	196.0 ± 6.3	12.8 ± 0.9	74.2 ± 1.9	<MRL
SC-12	35.7	70.1–94.5	329.6 ± 3.1	50.0 ± 28.5	43.3 ± 0.7	<MRL

Table B-5. (Continued).

Sampling point	Distance from RRWTP (km)	Depth of screened interval (m)	Sucralose	PFOS	PFOA	Tonalide
SC-1	0.8	33.5–45.7	307.8 ± 5.4	13.2 ± 0.1	9.5 ± 0.6	5.9 ± 0.5
SC-2	3.7	29.0–41.1	322.1 ± 160.8	55.1 ± 4.5	12.6 ± 5.9	18.4 ± 4.8
SC-3	8.4	27.4–39.6	1180.4 ± 158.8	20.5 ± 0.7	7.9 ± 3.3	109.0 ± 61.9
SC-5	13.1	32.0–50.3	3470.2 ± 1014.7	34.2 ± 5.7	10.6 ± 2.7	18.4 ± 19.2
SC-6	14.8	35.1–56.4	609.0 ± 17.3	40.2 ± 0.4	17.8 ± 0.7	71.6 ± 6.8
SC-7	18.0	42.7–61.0	1808.9 ± 57.5	49.3 ± 7.5	12.3 ± 9.4	92.4 ± 29.8
SC-8	20.0	61.0–91.4	109.4 ± 21.7	65.7 ± 2.1	14.8 ± 0.3	1.8 ± 0.3
SC-9	25.6	88.4–115.8	94.7 ± 31.4	8.9 ± 1.3	2.5 ± 0.3	4.9 ± 0.1
SC-10	27.2	91.4–112.8	71.0 ± 1.2	8.3 ± 0.6	2.5 ± 0.1	8.0 ± 3.4
SC-11	32.7	57.6–100.3	379.9 ± 23.6	47.3 ± 1.7	10.9 ± 0.3	12.4 ± 0.9
SC-12	35.7	70.1–94.5	179.1 ± 47.0	79.7 ± 4.1	13.9 ± 0.1	1.1 ± 0.5

Note: Values represent averages plus/minus one standard deviation.

<MRL means less than method reporting limit, a value that is arbitrarily set at 9 times the signal-to-noise ratio.

Table B-6. Concentrations of TOrCs in the Lower Santa Cruz River sediments (ng/g dry weight) for the six locations sampled in February 2013. See Table B-4 for downstream distances of sampling points.

Analyte	RRWTP	El Camino del Cerro	N. Silverbell Rd	N. Cortaro Rd	Heritage Park Dr	N. Trico Rd
Nonylphenol	101.46	85.55	110.3	117.73	254.1	148.12
Octylphenol	9.64	8.05	3.01	3.16	5.43	2.77
Caffeine	67.6	19.5	16	5.87	7.5	4.54
Trimethoprim	0.52	0.72	0.53	0.26	0.36	0.31
Carbamazepine	0.39	0.11	0.39	0.02	0.02	0.02
TCPP	2.83	2.73	2.75	1.63	1.38	1.3
Benzophenone	4.51	23.2	10.3	12.5	5.29	3.89
Benzotriazole	0.24	3.39	0.08	0.18	0.33	0.2
Diclofenac	0.56	<MRL	0.26	0.16	<MRL	0.16
Bisphenol A	0.24	1.25	1.13	0.7	0.17	0.42
PFDA	0.19	0.08	0.08	<MRL	0.06	0.07
PFOS	0.89	0.16	0.11	0.1	0.05	0.11
Triclocarban	3.72	2.41	0.92	1	0.54	1
Triclosan	3.68	2.73	0.57	1.49	<MRL	0.62

Note: <MRL means less than method reporting limit, a value that is arbitrarily set at 9 times the signal-to-noise ratio.

Only five of the fourteen compounds found in sediments were also detected in the liquid-phase sampling campaign. Sediment concentrations of four out of those five decreased with distance in the river (Figure B-7); NP was the lone exception. Of the same five compounds in river water samples, only the rate of decrease of PFOS with distance was statistically significant ($p < 0.05$ — Table B-2).

Figure B-7. Observed trace organic concentrations in SCR sediments vs. distance in the February 2013 sampling event. Concentrations are in ng of compound per g of dry sediment. Measurements correspond to surface sediment samples from the riverbed (0–2.5 cm depth).

Both NP and OP are present in water and sediments. Concentrations of NP (85–254 ng/g) and OP (2.8–9.6 ng/g) in the surface sediment layer (0–2.5 cm) were comparable to levels in the sediments of other effluent-dependent streams (Isobe et al. 2001; Liu et al. 2004). The results suggest that sorption may play an important role in the fate of

alkylphenols in the river due to their relatively high hydrophobicity (Isobe et al. 2001). Biodegradation of their parent compounds, APnEOs, may have contributed to NP and OP concentrations in sediment samples (Ahel et al. 1994a).

After NP, caffeine, which we did not attempt to measure in the river water, was the most abundant TOrC among those measured in SCR sediments (Table B-6). Despite its relatively high water solubility (and low D_{OW} , Table B-1), caffeine has been detected before in riverbed sediment samples at levels of the order of 1 μg per gram of organic carbon (Nilsen et al. 2007). In addition, caffeine attenuation has been measured in surface waters (Musolff et al. 2009). This suggests that caffeine partitions at detectable levels between water and sediment phases. On the other hand sucralose, which is also water-soluble, was not detected in sediments. BPA, PFOS and PFDA were present at values near their respective detection limits. Riverbed concentrations of TOrCs generally decreased with distance. It is difficult to associate the trends observed with sediment dynamics, due to the lack of information on sediment resuspension and redistribution in the river, especially during storm events but results suggest that this would be an important matter to pursue in further research.

B.3.6 Estrogenic Activity in Riverbed Sediments

Extractable estrogenic activities in the top (0–2.5 cm) and deeper (10.2–12.7 cm) sediment strata were measured during each sampling campaign in 2012 and 2013. Values were generally higher before (June) than immediately after (July) the intense summer rainfall period (Figure B-8). The data suggest that intense rainfall/runoff events are capable of attenuating sediment estrogenic levels throughout the sediment strata tested,

probably through sediment scour and redeposition (Williams et al. 1999). Lacher (1996) observed a general improvement in channel infiltration capacity following high flows in early March in the SCR. During the summer months, there was a general increase followed by a progressive reduction in the infiltration capacity of the streambed, as indicated by the length of the wetted reach of the streambed during dry weather flows. Storm flows scoured the upstream portion of the study reach and exhibited depositional behavior in the downstream end of the reach. Seasonal changes in sediment estrogenic activity may have a similar explanation.

Prior to the rainy season, the level of estrogenic activity in the top layer sediment at the sampling site 11 km downstream of the RRWTP outfall was $\sim 5\times$ times higher than the level in the lower sediment layer (Figure B-8). At the extreme downstream sampling site (37 km below RRWTP), extractable estrogenic activity in the lower sediment layer was $\sim 2\times$ that of the surface layer, indicating that estrogenic compounds are not degraded completely in the stream or, alternatively, that some estrogenic compounds adsorb to sediments closer to the outfalls and are redistributed with distance and depth in river sediments during storm events.

Figure B-8. Estrogenic activities as a function of position and time in riverbed sediment samples taken from the Santa Cruz River: (a) top layer sediment (top 2.5 cm); (b) lower layer sediment (10.2–12.7 cm depth).

B.4 Conclusions

The results presented show that some TOrCs, including biodegradable compounds (hypothesis 1) and those that contribute to estrogenic activity, are rapidly attenuated with distance of travel in the Santa Cruz River. Independent experiments indicate that the

attenuation of estrogenic compounds is due, at least in part, to indirect photolysis caused by formation of organic radicals from sunlight absorption (hypothesis 2). This attenuation mechanism is expected to play a role not only in effluent dependent streams, but also in natural bodies of water receiving wastewater treatment plant effluent. TOrCs that survive percolation to ground water generally have in common low biodegradation probabilities and low octanol–water distribution ratios. Evidence is presented that suggests that riverbed sediment quality, in terms of concentrations of hydrophobic TOrCs, is periodically affected by storm-related scouring during periods of heavy rainfall and runoff (hypothesis 3). Our results suggest that the resuspension and transport of sediments play an important role in the fate of TOrCs in rivers impacted by wastewater treatment. The sum of natural attenuation processes occurring during river transport in the Santa Cruz River, an effluent-dependent stream, and during percolation to local ground water, substantially reduce the concentrations of some TOrCs, providing potential benefit to the local ecosystem and human health of downstream communities that may utilize that water.

B.5 Acknowledgement

This work was supported by the University of Arizona Water, Environmental and Energy Solutions initiative co-managed by the Water Sustainability Program, Institute of the Environment, and Renewable Energy Network, grant number WEESGFY13SAEZ. The authors also wish to acknowledge funding from the National Institutes for Water Resources, grant number 2012AZ492B. This work was supported by the USDA National Institute of Food and Agriculture, Hatch project 230922. Thanks to Darryl Jones and Andrew Keller for sampling and experimental support. Thanks also to Rob Speir, Jason

Grodman, and Mike Silva from Pima County Regional Wastewater Reclamation Department for assistance in collection of groundwater samples. The authors also wish to thank the anonymous peer reviewers for providing thoughtful comments that improved the paper.

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APPENDIX B1: Supplementary Materials for APPENDIX B

Figure B1-1. Record of flows at Tucson area USGS gauging stations in the Santa Cruz River during the period of study — February 2012 to February 2013. For station locations, see Figure B-1. Comparison shows that (i) the river is dry upstream of the RRWTP (a), except during rainfall events and (ii) nearly 60% of the flow measured at Cortaro Road (b) infiltrates in the riverbed between Cortaro Road and Trico Road (c).

Table B1-1. Dissolved concentrations of TOrCs at sampling sites in the Lower Santa Cruz River. The positions of sampling points are shown in Figure B-2 (values represent averages plus/minus one standard deviation (ng/L) based on three sampling campaigns during 2011).

Sampling point	Carbamezapine	DEET	Sulfamethoxazole	TCEP	Tonalide	Fluoxetine
Roger Rd Outfall	343.5 ± 22.2	786.4 ± 127.5	1308.9 ± 436.4	326.1 ± 24.7	39.2 ± 4.8	41.9 ± 5.5
SC-1R	419.1 ± 122.4	764.0 ± 135.0	1446.4 ± 477.5	319.9 ± 13.5	28.6 ± 7.6	29.7 ± 1.9
SC-2R	321.9 ± 149.5	739.2 ± 95.9	1390.0 ± 548.1	352.0 ± 52.8	20.8 ± 7.0	25.2 ± 4.0
Ina Rd Outfall	354.4 ± 25.2	346.6 ± 168.1	775.0 ± 409.8	318.9 ± 39.3	28.7 ± 8.1	70.7 ± 19.9
SC-3R	369.4 ± 90.7	511.9 ± 174.5	1420.1 ± 657.5	325.5 ± 44.4	23.5 ± 5.9	35.4 ± 4.5
SC-4R	316.4 ± 77.8	308.4 ± 6.3	759.5 ± 96.9	306.5 ± 5.5	23.2 ± 3.1	49.7 ± 13.4
SC-5R	390.7 ± 103.7	415.0 ± 96.4	1152.8 ± 329.5	323.5 ± 42.3	22.4 ± 2.4	40.2 ± 19.9
SC-6R	365.6 ± 75.3	467.2 ± 222.6	1095.0 ± 283.6	342.5 ± 70.3	21.0 ± 3.4	34.4 ± 15.4
SC-7R	389.4 ± 108.4	454.3 ± 149.8	1207.1 ± 403.5	329.0 ± 66.7	18.6 ± 1.8	35.1 ± 22.2
SC-8R	398.1 ± 98.7	474.7 ± 23.9	1398.4 ± 437.8	288.6 ± 3.9	17.9 ± 1.6	24.9 ± 4.8
SC-9R	399.6 ± 126.5	399.3 ± 80.8	1460.8 ± 483.6	282.4 ± 35.6	20.3 ± 7.5	23.6 ± 10.2
SC-10R	434.0 ± 113.9	401.0 ± 96.5	1545.6 ± 296.2	301.8 ± 21.9	18.8 ± 5.1	20.1 ± 7.2
SC-11R	445.7 ± 139.6	367.9 ± 131.7	1571.7 ± 483.4	278.0 ± 8.9	20.3 ± 7.4	14.0 ± 5.9
SC-12R	361.9 ± 105.7	319.9 ± 126.8	1522.6 ± 589.0	300.0 ± 29.5	15.2 ± 5.8	11.9 ± 4.6

Table B1-1. (Continued).

Sampling point	Trimethoprim	Primidone	Iopromide	Sucralose	PFOS	PFOA
Roger Rd Outfall	547.4 ± 174.5	109.7 ± 40.7	239.1 ± 68.0	2804.3 ± 991.3	19.9 ± 23.2	11.0 ± 8.0
SC-1R	596.8 ± 167.3	112.9 ± 37.7	229.9 ± 40.4	2726.6 ± 687.1	11.9 ± 13.0	5.9 ± 1.2
SC-2R	465.7 ± 300.4	121.0 ± 32.1	204.1 ± 137.5	3029.0 ± 968.0	37.3 ± 49.6	14.0 ± 7.6
Ina Rd Outfall	310.4 ± 71.6	160.6 ± 15.5	96.2 ± 49.3	3886.5 ± 1924.8	9.2 ± 4.2	11.8 ± 2.5
SC-3R	381.8 ± 199.0	137.0 ± 39.4	180.2 ± 92.5	4661.9 ± 2822.1	15.6 ± 14.6	12.2 ± 5.5
SC-4R	247.9 ± 139.8	166.3 ± 33.3	104.5 ± 86.6	4632.8 ± 1495.3	18.3 ± 14.6	9.5 ± 2.5
SC-5R	323.8 ± 127.6	156.8 ± 20.3	137.1 ± 54.1	4091.6 ± 1094.6	18.0 ± 19.8	11.2 ± 3.4
SC-6R	318.4 ± 145.4	152.0 ± 7.1	81.5 ± 52.5	3690.8 ± 1451.7	19.3 ± 24.0	13.2 ± 7.2
SC-7R	347.6 ± 139.1	148.0 ± 14.2	88.0 ± 35.9	3647.6 ± 1141	21.2 ± 24.8	10.9 ± 2.6
SC-8R	242.4 ± 71.8	177.4 ± 26.3	90.0 ± 52.2	3584.8 ± 1021.1	11.7 ± 4.7	7.6 ± 4.4
SC-9R	329.9 ± 189.9	172.9 ± 19.0	77.0 ± 33.3	3956.3 ± 1071.6	18.0 ± 13.8	11.2 ± 1.4
SC-10R	313.7 ± 126.7	175.2 ± 17.0	59.9 ± 41.2	3983.0 ± 789.9	12.8 ± 10.3	10.9 ± 1.7
SC-11R	275.7 ± 147.7	178.4 ± 10.7	81.9 ± 31.7	3996.5 ± 808.5	10.3 ± 2.6	10.4 ± 1.1
SC-12R	208.9 ± 158.4	160.2 ± 17.6	72.2 ± 25.9	3214.0 ± 197.5	8.1 ± 3.9	9.5 ± 3.7

Table B1-2. Concentrations of TOrCs in the Lower Santa Cruz River monitoring wells (values represent averages plus/minus one standard deviation (ng/L)).

Sampling point	Carbamazepine	Sulfamethoxazole	Primidone	Iopromide	Sucralose	PFOS	PFOA	Tonalide
SC-1W	191.2 ± 3.5	7.9 ± 0.1	134.4 ± 2.9	<MRL	307.8 ± 5.4	13.2 ± 0.1	9.5 ± 0.6	5.9 ± 0.5
SC-2W	268.5 ± 55.3	15.2 ± 6.6	142.3 ± 10.4	1.4 ± 1.3	322.1 ± 160.8	55.1 ± 4.5	12.6 ± 5.9	18.4 ± 4.8
SC-3W	369.1 ± 110.3	260.8 ± 81.1	184.9 ± 0.4	22.7 ± 4.1	1180.4 ± 158.8	20.5 ± 0.7	7.9 ± 3.3	109.0 ± 61.9
SC-5W	312.0 ± 96.4	55.0 ± 43.6	172.4 ± 33.5	2.0 ± 0.5	3470.2 ± 1014.7	34.2 ± 5.7	10.6 ± 2.7	18.4 ± 19.2
SC-6W	374.5 ± 2.6	31.0 ± 1.5	227.8 ± 3.0	<MRL	609.0 ± 17.3	40.2 ± 0.4	17.8 ± 0.7	71.6 ± 6.8
SC-7W	259.2 ± 57.2	62.1 ± 1.0	193.4 ± 4.0	1.4 ± 0.3	1808.9 ± 57.5	49.3 ± 7.5	12.3 ± 9.4	92.4 ± 29.8
SC-8W	202.4 ± 0.6	13.2 ± 2.3	59.5 ± 2.8	<MRL	109.4 ± 21.7	65.7 ± 2.1	14.8 ± 0.3	1.8 ± 0.3
SC-9W	7.5 ± 0.4	9.0 ± 1.9	9.2 ± 0.1	<MRL	94.7 ± 31.4	8.9 ± 1.3	2.5 ± 0.3	4.9 ± 0.1
SC-10W	12.3 ± 0.2	6.4 ± 0.1	12.4 ± 0.9	<MRL	71.0 ± 1.2	8.3 ± 0.6	2.5 ± 0.1	8.0 ± 3.4
SC-11W	196.0 ± 6.3	12.8 ± 0.9	74.2 ± 1.9	<MRL	379.9 ± 23.6	47.3 ± 1.7	10.9 ± 0.3	12.4 ± 0.9
SC-12W	329.6 ± 3.1	50.0 ± 28.5	43.3 ± 0.7	<MRL	179.1 ± 47.0	79.7 ± 4.1	13.9 ± 0.1	1.1 ± 0.5

Note: <MRL means less than method reporting limit, a value that is arbitrarily set at 9:1 the signal-to-noise ratio.

Table B1-3. Concentrations of TOrCs in the Santa Cruz River sediment samples from the February 2013 sampling event (ng/g dw).

Sampling point	Agua Nueva WRF	El Camino del Cerro	N. Silverbell Rd	N. Cortaro Rd	Heritage Park Dr	N. Trico Rd
Nonylphenol	101.46	85.55	110.3	117.73	254.1	148.12
Octylphenol	9.64	8.05	3.01	3.16	5.43	2.77
Caffeine	67.6	19.5	16	5.87	7.5	4.54
Trimethoprim	0.52	0.72	0.53	0.26	0.36	0.31
Carbamazepine	0.39	0.11	0.39	0.02	0.02	0.02
TCPP	2.83	2.73	2.75	1.63	1.38	1.3
Benzophenone	4.51	23.2	10.3	12.5	5.29	3.89
Benzotriazole	0.24	3.39	0.08	0.18	0.33	0.2
Diclofenac	0.56	<MRL	0.26	0.16	<MRL	0.16
Bisphenol A	0.24	1.25	1.13	0.7	0.17	0.42
PFDA	0.19	0.08	0.08	<MRL	0.06	0.07
PFOS	0.89	0.16	0.11	0.1	0.05	0.11
Triclocarban	3.72	2.41	0.92	1	0.54	1
Triclosan	3.68	2.73	0.57	1.49	<MRL	0.62

Note: <MRL means less than method reporting limit, a value that is arbitrarily set at 9:1 the signal-to-noise ratio.

Statistical Parameters

The statistical correlations presented in Tables B-2 and B-3 of the manuscript correspond to least-squared error linear fits. For a collection of data y_i vs, x_i , the linear fit is represented by

$$\hat{y} = ax + b \quad \text{Eq (B1-1)}$$

where $\hat{y}$ represents fitted value. The total squared error is defined by

$$\text{TSE} = \sum_i (y_i - \hat{y}_i)^2 \quad \text{Eq (B1-2)}$$

The values of a and b in the correlation are chosen to minimize TSE. The goodness of the fit can be represented by the correlation coefficient (as in Table B-2), defined by

$$R^2 = 1 - \frac{\text{TSE}}{\text{TSD}} \quad \text{Eq (B1-3)}$$

where TSD is the total square deviation from the mean of the set of values y_i , $\bar{y}_i$,

$$\text{TSD} = \sum_i (y_i - \bar{y}_i)^2 \quad \text{Eq (B1-4)}$$

An important parameter is the standardized coefficient (as in Table B-3), which represents the change (in number of standard deviations) of the dependent variable (y) induced by a change of one standard deviation of the independent variable (x). The standardized coefficient (β) is the fitted value of a (slope of the correlation) for the least-squared error fit

$$\hat{y} = \beta x' + b' \quad \text{Eq (B1-5)}$$

where

$$x' = \frac{x - \bar{x}}{s_x}$$

Eq (B1-6)

where $\bar{x}$ and s_x are the mean and standard deviation of the set of x values.

APPENDIX C: Photolysis of Fe(III) Hydroxo Complexes in Aqueous Solutions

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Abstract

A kinetic model in which aquahydroxo complexes of Fe^{3+} and their hydrolysis products are disproportionated to Fe^{2+} and hydroxyl radicals in ultraviolet light is proposed and tested experimentally. The model accounts for Fenton-like reactions and direct photolysis of H_2O_2 formed by radical recombination. Iron speciation and photochemical parameters, including the molar absorptivities of light-absorbing species and the quantum yields of Fe^{3+} and FeOH^{2+} hydrolysis (hydroxyl radical production/photon absorption) were experimentally validated. However, the predicted, time-dependent Fe^{2+} concentrations during Fe(III)/UV photolysis were much lower than measured. Potential explanations include overestimation of Fe^{2+} oxidation by hydroxyl radicals. When UV irradiation was discontinued, both measured and simulated Fe^{2+} levels decreased immediately as a consequence of reaction with residual H_2O_2 . Simulated Fe^{2+} trajectories were accurate when hydrogen peroxide was initially present at sufficiently high concentrations—so that Fenton's reactions overwhelmed the photolytic pathways. The kinetic model also accurately predicts the trajectory of Fe^{2+} when the initial concentration of ferrous iron is large. The nature of elements missing from the proposed model that would account for residual deficiencies is discussed.

Keywords: advanced oxidation; photolysis; ferric hydroxo complexes; hydroxyl radical; mechanism.

C.1 Introduction

Photolytic disproportionation reactions involving aqua-Fe(III) complexes have received considerable attention as means for generating hydroxyl radicals ($\cdot\text{OH}$, reactions C-1 to C-3) (Baxendale and Magee 1955; Adamson et al. 1962; Langford and Carey 1975; Pozdnyakov et al. 2000). The ability of hydroxyl radicals to destroy trace organic compounds in water, treated wastewater and industrial waste is widely appreciated (e.g. Rosario-Ortiz et al. 2010; Matilainen and Sillanpää 2010; Rodríguez et al. 2012; Prieto-Rodríguez et al. 2013; Pešoutová et al. 2014). Once formed, the recombination of hydroxyl radicals to form hydrogen peroxide (H_2O_2 , reaction C-4) is inevitable, providing all the elements of the proposed photo-Fenton mechanism (Faust and Hoigné 1990; Zepp et al. 1992; Kim and Vogelpohl 1998). These works frequently used $\cdot\text{OH}$ scavengers in short term irradiation experiments to avoid oxidation of Fe^{2+} by $\cdot\text{OH}$ and simplify the reaction mechanism while establishing reaction quantum yields (e.g. Logan 1990; Kawaguchi and Inagaki 1993; Benkelberg and Warneck 1995; Nadtochenko and Kiwi 1998; Joseph et al. 2001; Rodríguez et al. 2002; Lee and Yoon 2004a, 2004b). In those cases, the full range of reactions that determine the trajectory of Fe^{2+} concentration was not observed.

The environmental relevance of these reactions arises from the non-specific reactions of hydroxyl and other inorganic radicals with dissolved organic compounds, including a variety of trace organics of anthropogenic origin that routinely survive municipal wastewater treatment processes (e.g. Andreozzi et al. 2006; Rodríguez et al. 2007; Jin et al. 2014; Spasiano et al. 2014).

Photo-Fenton nomenclature covers treatment strategies based on the addition of iron and peroxide under ultraviolet irradiation, taking advantage of both H_2O_2 and aqua-Fe(III) species photolyses and iron cycling via reaction with peroxide to produce hydroxyl radicals (e.g. Kavitha and Palanivelu 2004; Badawy et al. 2006; Shemer et al. 2006; Méndez-Arriaga et al. 2010). The advantage of photo-Fenton processes is generally kinetic since hydroxyl radicals are produced via aqua-Fe(III) and H_2O_2 photolyses as well as the reaction of Fe^{2+} with supplemental H_2O_2 . The kinetics and mechanism of photo-Fenton processes are less established than those of Fenton reactions and Fe(III) photolysis alone despite successful studies by Einschlag et al. (2013) and others. Successful simulation of photo-Fenton processes under natural conditions necessarily involves pathways critical to both Fenton's mechanism, and aqua-Fe(III) photolysis, hydroxyl radical quenching by H_2O_2 and perhaps other radical interactions leading the formation of carbonate and sulfate radicals.

A kinetic model for photolysis of ferric-hydroxo, -sulfate and -chloride complexes under black light was proposed and validated by Machulek et al. (2009). Their model, which consists of (i) photolyses of FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, FeCl^{2+} and FeSO_4^+ and (ii) a Fenton-like mechanism in the presence of sulfate and chloride in acidic solutions, fit experimental

data for Fe(II) formation under various conditions satisfactorily. Another Fe(III)/UV photolysis kinetic model was established and tested by Wang and Liu (2014). Besides integrating photolysis of FeOH^{2+} with Fenton-like systems, those authors also considered the photochemical oxidation of Fe^{2+} by dissolved oxygen.

Here we propose and evaluate a kinetic model combining the photolyses of H_2O_2 and aqua-Fe(III) species with Fenton's reactions. The model is supported by bench-scale measurements under controlled conditions. Work is restricted, for example to irradiance at 254 nm, and iron is provided as ferric perchlorate ($\text{Fe}(\text{ClO}_4)_3$), since the perchlorate anion is viewed as chemically inert under these circumstances.

C.2 Materials and Methods

C.2.1 Chemicals

All chemicals were reagent grade and used without further purification, including iron (III) perchlorate hydrate ($\text{Fe}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$, Aldrich, crystalline, low chloride), iron (II) perchlorate hydrate ($\text{Fe}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$, Aldrich, 98%), perchloric acid (HClO_4 , Ricca Chemical, 2.00 N aqueous), sodium perchlorate (NaClO_4 , Sigma-Aldrich, $\geq 98.0\%$ ACS grade), hydroxylamine hydrochloride (Sigma-Aldrich, ReagentPlus[®], 99%), 1,10-phenanthroline monohydrate (Fluka, for the spectrophotometric determination of Fe, Pd, V, $\geq 99.0\%$), ammonium acetate ($\text{NH}_4\text{CH}_3\text{CO}_2$, Sigma-Aldrich, BioXtra, $\geq 98\%$), glacial acetic acid (Fisher, Certified ACS), *p*-cresol (Acros, 99+%), hydrogen peroxide (H_2O_2 , Fisher Scientific, 30% ACS grade), titanium (IV) sulfate (Pfaltz&Bauer, 30%) and nitric acid solution in water (Acros, 68-70% ACS grade). Milli-Q water (resistivity $\geq 18.0 \text{ M}\Omega \text{ cm}$; Barnstead NANOpure II system) was used in solution preparations.

C.2.2 Solution Preparation

All iron solutions were prepared immediately before the experiments as follows: (1) Fe(III) and Fe(II) stock solutions were prepared by dissolving ferric and ferrous salts into a few milliliters of Milli-Q water-diluted HClO_4 solution (0.1 N); (2) after measuring the iron content of stock solutions (described later), appropriate volumes of the Fe(III) and Fe(II) (if needed) stock solutions were added to the reactor to reach the desired total volume and iron concentrations; (3) 2.0 N HClO_4 was added to adjust pH; and (4) NaClO_4 salt was added to achieve 0.1 M ionic strength. In experiments where *p*-cresol was utilized as a $\cdot\text{OH}$ scavenger, a freshly prepared 50 mM *p*-cresol aqueous solution was added to make the initial concentration of *p*-cresol 100 μM . After preparation, solutions were stirred for 15 minutes before UV irradiation began. For photo-Fenton experiments, H_2O_2 was introduced immediately following exposure to light unless otherwise indicated.

C.2.3 Experimental Setup and Procedure

A STER-L-RAY[®] low-pressure UV ($\lambda = 254 \text{ nm}$) lamp (G10T5 1/2L, ozone free) was used for irradiation in this study. A cylindrical glass batch reactor (14-cm inner diameter, 300 mL volume with 2-cm light path length) with continuous agitation using a HI 190M-1 magnetic mini-stirrer (Hanna Instruments) and 6×25 mm PTFE magnetic stir bar was employed. The reactor was set on an optical table 20 cm below the low-pressure UV lamp (Figure C-1). At this distance, the average intensity at the fluid surface was 780 $\mu\text{W}/\text{cm}^2$ —measured using a UV Power Meter (Model C8026, Hamamatsu Photonics K.K.) with 254 nm sensor (Model H8025-254).

Figure C-1. Front view (top) and top view (bottom) of irradiation experiments setup used in this study (not to scale).

During the experiments, 1-mL samples were periodically withdrawn for iron analysis. Samples were also taken for determinations of *p*-cresol and H₂O₂. All samples were analyzed immediately after collection. The reactor temperature was maintained at 25 °C, and solution pH was continuously monitored (VWR, SP70P).

All glassware was washed with 1% nitric acid aqueous solution first, then rinsed 3 to 5 times with Milli-Q water, and baked overnight at 550 °C using a Thermolyne 6000 Muffle Furnace (Dubuque, IA). Quartz cuvettes (Perkin Elmer, Quartz SUPRASIL Macro) used in fluorescence and UV/Vis spectroscopic analyses were pre-soaked in 3% nitric acid/water before use.

C.2.4 Analytical

The *o*-phenanthroline colorimetric method (Tamura et al. 1974) was used to measure Fe(II) and Fe(III) ($[\text{Fe(III)}] = [\text{Fe}]_{\text{tot}} - [\text{Fe(II)}]$). During the experiments, 1-mL samples were added to 20-mL borosilicate glass scintillation vials containing 2.5-mL Milli-Q water, 1-mL ammonium acetate buffer solution (250 g $\text{NH}_4\text{CH}_3\text{CO}_2$ dissolved in 150-mL Milli-Q water plus 700-mL glacial acetic acid) and 0.5-mL phenanthroline solution (100 mg 1,10-phenanthroline monohydrate solids dissolved in 100-mL Milli-Q water) for Fe(II) analysis. Absorbance of the assay mixture was measured by a Thermo Scientific Genesys 10s UV-Vis spectrophotometer at 510 nm ($\epsilon = 11,000 \text{ M}_{\text{Fe(II)}}^{-1} \text{ cm}^{-1}$). Next, 0.1-mL of concentrated hydroxylamine hydrochloride solution (200 g/L) was spiked into the assay mixture to reduce all Fe(III) to Fe(II) before the absorbance of the assay mixture was again measured (same method) to obtain the total iron concentration (i.e.— $[\text{Fe(II)}] = [\text{Fe}]_{\text{tot}}$ in this case). Iron absorption spectra from 200 to 380 nm were determined using the same UV-Vis spectrophotometer.

p-Cresol was analyzed using a PerkinElmer LS 55 fluorescence spectrophotometer equipped with a pulsed xenon lamp to reduce the photobleaching effect. The inner filter effect (IFE) caused by light absorption and reabsorption of light-absorbing compounds was corrected by a mathematical model (MacDonald et al. 1997) that takes into account the sample absorption spectrum. Sample spectra were obtained by UV-Vis spectrophotometry. All fluorescence intensities (arbitrary unit, AU) were corrected by the IFE model before data analysis.

H₂O₂ concentrations were determined using the titanium sulfate colorimetric method (Boltz and Holwell 1978), which has a detection range from 1.5×10^{-6} to 10^{-1} M, using assay dilution factors ranging from 0.98 to 0.007. Absorbance of the complex formed from the reaction between H₂O₂ and titanium sulfate was measured using the UV-Vis spectrophotometer at 407 nm ($\epsilon = 730 \text{ M}_{\text{H}_2\text{O}_2}^{-1} \text{ cm}^{-1}$).

C.3 Modeling

C.3.1 Kinetic Model

Reactions that comprise the kinetic model, rate constants for all elementary reactions and equilibrium constants for reversible reactions are provided in Table C-1. The kinetic model accounts for: (1) photolyses of Fe³⁺, Fe(OH)²⁺, and H₂O₂; (2) Fenton-like reactions—i.e. Fe(III)/H₂O₂ and related reactions; and (3) reactions of *p*-cresol and its oxidation by-products with •OH.

The initial step of this system was used to study the photolysis of Fe³⁺ and Fe(OH)²⁺ alone (P1 and P2 in Table C-1). The rate of reduction of Fe(III) via photolysis is given by

$$\frac{d[\text{Fe(III)}]_{\text{photo}}}{dt} = -(\Phi_{\text{Fe}} f_{\text{Fe}} + \Phi_{\text{FeOH}} f_{\text{FeOH}}) I_0 (1 - 10^{-\text{Abs}_{254}}) \quad \text{Eq (C-1)}$$

Φ_{Fe} and Φ_{FeOH} are quantum yields (hydroxyl radical production/photon absorption, mol/Ein) for the hydrolytic disproportionation of Fe³⁺ and Fe(OH)²⁺ at 254 nm, respectively; I_0 is the average UV₂₅₄ fluence rate ($\text{EinL}^{-1} \text{s}^{-1}$); f_{Fe} and f_{FeOH} are the fractions of light absorbed by Fe³⁺ and FeOH²⁺ and Abs₂₅₄ is the total solution absorbance at 254 nm.

The UV₂₅₄ fluence rate is calculated from

$$I_o = \frac{A_R \lambda E}{V_R \hbar c N_a} \quad \text{Eq (C-2)}$$

where A_R and V_R are reactor surface area (m²) and volume (L), λ is incident light wavelength (m), E is incident light intensity (W/m²), $\hbar$ is Planck's constant (kg·m²·s⁻¹/photon), c is speed of light (m/s) and N_a is Avogadro constant (photons/Ein).

Table C-1. Summary of reaction rate and equilibrium constants for kinetic modeling of Fe(III) photolysis at 25 °C.

ID	Reactions	Rate constants	Reference
E1	$\text{Fe}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{FeOH}^{2+} + \text{H}^+$	$K_1 = 2.9 \times 10^{-3} \text{ M}$	De Laat and Gallard 1999
E2	$\text{Fe}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_2^+ + 2\text{H}^+$	$K_2 = 7.62 \times 10^{-7} \text{ M}^2$	De Laat and Gallard 1999
E3	$2\text{Fe}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \text{Fe}_2(\text{OH})_2^{4+} + 2\text{H}^+$	$K_3 = 0.8 \times 10^{-3} \text{ M}$	De Laat and Gallard 1999
E4	$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \leftrightarrow \text{Fe}(\text{HO}_2)^{2+} + \text{H}^+$	$K_4 = 3.1 \times 10^{-3}$	De Laat and Gallard 1999
E5	$\text{FeOH}^{2+} + \text{H}_2\text{O}_2 \leftrightarrow \text{Fe}(\text{OH})(\text{HO}_2)^+ + \text{H}^+$	$K_5 = 2.0 \times 10^{-4}$	De Laat and Gallard 1999
P1	$\text{Fe}^{3+} + \text{H}_2\text{O} + h\nu \rightarrow \text{Fe}^{2+} + \cdot\text{OH} + \text{H}^+$	$\Phi_{\text{Fe}} = 0.046 \text{ mol/Ein}$	Lee and Yoon 2004a
P2	$\text{FeOH}^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \cdot\text{OH}$	$\Phi_{\text{FeOH}} = 0.69 \text{ mol/Ein}$	Lee and Yoon 2004a
P3	$\text{H}_2\text{O}_2 + h\nu \rightarrow \cdot\text{OH} + \cdot\text{OH}$	$\Phi_{\text{H}_2\text{O}_2} = 0.50 \text{ mol/Ein}$	Baxendale and Wilson 1957
R1	$\text{Fe}(\text{HO}_2)^{2+} \rightarrow \text{Fe}^{2+} + \text{HO}_2\cdot$	$k_1 = 2.7 \times 10^{-3} \text{ s}^{-1}$	De Laat and Gallard 1999
R2	$\text{Fe}(\text{OH})(\text{HO}_2)^+ \rightarrow \text{Fe}^{2+} + \text{HO}_2\cdot + \text{OH}^-$	$k_2 = 2.7 \times 10^{-3} \text{ s}^{-1}$	De Laat and Gallard 1999
R3	$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^-$	$k_3 = 6.3 \times 10^1 \text{ M}^{-1}\text{s}^{-1}$	De Laat and Gallard 1999
R4	$\text{Fe}^{2+} + \cdot\text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$	$k_4 = 3.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	De Laat and Gallard 1999
R5	$\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2\cdot + \text{H}_2\text{O}$	$k_5 = 3.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	De Laat and Gallard 1999
R6	$\text{Fe}^{2+} + \text{HO}_2\cdot \rightarrow \text{Fe}(\text{HO}_2)^{2+}$	$k_6 = 1.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	De Laat and Gallard 1999
R7	$\text{Fe}^{2+} + \text{O}_2^{\cdot-} + \text{H}^+ \rightarrow \text{Fe}(\text{HO}_2)^{2+}$	$k_7 = 1.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	De Laat and Gallard 1999
R8	$\text{Fe}(\text{III}) + \text{HO}_2\cdot \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+$	$k_8 < 2.0 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$	De Laat and Gallard 1999
R9	$\text{Fe}(\text{III}) + \text{O}_2^{\cdot-} \rightarrow \text{Fe}^{2+} + \text{O}_2$	$k_9 = 5.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	De Laat and Gallard 1999
R10	$\text{HO}_2\cdot \rightarrow \text{O}_2^{\cdot-} + \text{H}^+$	$k_{10} = 1.58 \times 10^5 \text{ s}^{-1}$	De Laat and Gallard 1999
R10r	$\text{O}_2^{\cdot-} + \text{H}^+ \rightarrow \text{HO}_2\cdot$	$k_{10r} = 1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	De Laat and Gallard 1999
R11	$\text{HO}_2\cdot + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k_{11} = 8.3 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	De Laat and Gallard 1999
R12	$\text{HO}_2\cdot + \text{O}_2^{\cdot-} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^-$	$k_{12} = 9.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	De Laat and Gallard 1999
R13	$\cdot\text{OH} + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O} + \text{O}_2$	$k_{13} = 0.71 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	De Laat and Gallard 1999
R14	$\cdot\text{OH} + \text{O}_2^{\cdot-} \rightarrow \text{OH}^- + \text{O}_2$	$k_{14} = 1.01 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	De Laat and Gallard 1999
R15	$\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$	$k_{15} = 5.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	De Laat and Gallard 1999
P4	$p\text{-cresol} + h\nu \rightarrow \text{products}$	$\Phi_{\text{PC}} = 0.034 \text{ mol/Ein}$	Zhang et al. 2016
R16	$\cdot\text{OH} + p\text{-cresol} \rightarrow 4\text{MC}$	$k_{16} = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. 1988
P5	$4\text{MC} + h\nu \rightarrow \text{products}$	$\epsilon_{4\text{MC}} = 310 \text{ M}^{-1}\text{cm}^{-1}$	Zhang et al. 2016
R17	$\cdot\text{OH} + 4\text{MC} \rightarrow 4\text{MB}$	$\Phi_{\text{PC}} = 0.007 \text{ mol/Ein}$ $k_{17} = 1.6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Gohn and Getoff 1977

Table C-1. (Continued).

ID	Reactions	Rate constants	Reference
R18	$\cdot\text{OH} + 4\text{MB} \rightarrow 3\text{MM}^-$	$k_{18} = 2.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Zhang et al. 2016
R19	$\cdot\text{OH} + 3\text{MM}^- \rightarrow \text{L}^- + 2\text{Ox}^- (\text{Ox}^{2-})$	$k_{19} = 5.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Kang et al. 2002
R20	$\cdot\text{OH} + \text{L}^- \rightarrow \text{HA} (\text{A}^-) + \text{CO}_2 + \text{H}_2\text{O}$	$k_{20} = 3.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. 1988
R21	$\cdot\text{OH} + \text{Ox}^- \rightarrow \text{Ox}^{\cdot-} + \text{H}_2\text{O}$	$k_{21} = 4.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. 1988
R22	$\cdot\text{OH} + \text{Ox}^{2-} \rightarrow \text{Ox}^{\cdot-} + \text{OH}^-$	$k_{22} = 7.7 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. 1988
R23	$\text{Ox}^{\cdot-} + \text{Ox}^{\cdot-} \rightarrow \text{Ox}^- (\text{Ox}^{2-}) + 2\text{CO}_2$	$k_{23} = 5.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Ershov et al. 2008
R24	$\cdot\text{OH} + \text{HA} \rightarrow \text{F}^- + \text{CO}_2 + \text{H}_2\text{O}$	$k_{24} = 1.23 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Sun and Saeys 2008
R25	$\cdot\text{OH} + \text{A}^- \rightarrow \text{F}^- + \text{CO}_2 + \text{OH}^-$	$k_{25} = 8.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. 1988
R26	$\cdot\text{OH} + \text{F}^- \rightarrow \text{CO}_2 + \text{H}_2\text{O}$	$k_{26} = 9.77 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Sun and Saeys 2008
E6	$\text{Ox}^- \leftrightarrow \text{Ox}^{2-} + \text{H}^+$	$K_6 = 1.78 \times 10^{-4} \text{ M}$	Benjamin 2002
E7	$\text{HA} \leftrightarrow \text{A}^- + \text{H}^+$	$K_7 = 2.92 \times 10^{-5} \text{ M}$	Benjamin 2002

Note: 4MC = 4-methylcatechol, 4MB = 4-methylbenzoquinone, 3MM⁻ = deprotonated 3-methyl-muconic acid, L⁻ = lactate ion, Ox⁻ (Ox²⁻) = hydrogen oxalate ion (oxalate ion), HA (A⁻) = acetic acid (acetate ion), Ox^{·-} = oxalate radical, F⁻ = formate ion.

All equilibrium constants are conditional equilibrium constants at ionic strength = 0.1 M.

Reversible reactions (E1 to E7) are assumed to reach equilibrium instantaneously.

Fractions of light absorbed by the Fe^{3+} and FeOH^{2+} are

$$f_{\text{Fe}} = \frac{\varepsilon_{\text{Fe}}[\text{Fe}^{3+}]\ell}{\text{Abs}_{254}} \quad \text{Eq (C-3)}$$

$$f_{\text{FeOH}} = \frac{\varepsilon_{\text{FeOH}}[\text{FeOH}^{2+}]\ell}{\text{Abs}_{254}} \quad \text{Eq (C-4)}$$

where ε_{Fe} and $\varepsilon_{\text{FeOH}}$ are molar absorptivities ($\text{M}^{-1}\text{cm}^{-1}$) of Fe^{3+} and Fe(OH)^{2+} at 254 nm, respectively, and ℓ is the UV path length (cm). The total solution absorbance is then

$$\text{Abs}_{254} = \sum \varepsilon_i[i] \ell \quad \text{Eq (C-5)}$$

ε_i is the total molar absorptivity ($\text{M}^{-1}\text{cm}^{-1}$) at 254 nm including light absorption by Fe^{3+} , FeOH^{2+} , Fe(OH)_2^+ , $\text{Fe}_2(\text{OH})_2^{4+}$, $\text{Fe(HO}_2)^{2+}$, $\text{Fe(OH)(HO}_2)^+$, Fe^{2+} , Na^+ , ClO_4^- , H_2O_2 , *p*-cresol or $\cdot\text{OH}$ oxidation by-products of *p*-cresol (i.e.—4MC and 4MB). Except for $\varepsilon_{4\text{MC}}$ ($310 \text{ M}^{-1}\text{cm}^{-1}$; Zhang et al. 2016), $\varepsilon_{4\text{MB}}$ ($2100 \text{ M}^{-1}\text{cm}^{-1}$; Waite 1976; Jongberg et al. 2011), molar extinction coefficients are as provided in Table C1-1.

Once $\cdot\text{OH}$ is produced, H_2O_2 will be formed from radical-radical extinction (R15), which has a reported rate constant of $5.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. The in this way, the production of hydrogen peroxide converts the Fe(III) photolysis process initially present to a photo-Fenton process, although the concentrations of H_2O_2 are expected to remain low throughout. The overall process becomes a combination of three coincident $\cdot\text{OH}$ generation mechanisms: Fe(III) photolysis, H_2O_2 photolysis and Fenton-like radical generation. In this study, the Fenton-like mechanism represented in Table C-1 (E1 – 5 and R1 – 15) was taken from De Laat and Gallard (1999). In a subset of the experiments

conducted here, *p*-cresol was used as a radical scavenger. In those cases, the mechanism of *p*-cresol oxidation by $\cdot\text{OH}$ (Zhang et al. 2016) was integrated into the kinetic model.

According to the mechanism provided in Table C-1, rate equations for Fe(III) species, Fe^{2+} (at the pH of this study, $[\text{Fe}^{2+}] = [\text{Fe(II)}]$), H_2O_2 , *p*-cresol and $\cdot\text{OH}$ can be expressed in terms of the following set of differential equations:

$$\begin{aligned} \frac{d[\text{H}_2\text{O}_2]}{dt} = & -\Phi_{\text{H}_2\text{O}_2} f_{\text{H}_2\text{O}_2} I_0 (1 - 10^{-\text{Abs}_{254}}) - k_3 [\text{H}_2\text{O}_2] [\text{Fe}^{2+}] - k_5 [\text{H}_2\text{O}_2] [\cdot\text{OH}] \\ & + k_{11} [\text{HO}_2\cdot] [\text{HO}_2\cdot] + k_{12} [\text{O}_2^{\cdot-}] [\text{HO}_2\cdot] + k_{15} [\cdot\text{OH}] [\cdot\text{OH}] \end{aligned} \quad \text{Eq (C-6)}$$

$$\begin{aligned} \frac{d[\cdot\text{OH}]}{dt} = & (2\Phi_{\text{H}_2\text{O}_2} f_{\text{H}_2\text{O}_2} + \Phi_{\text{Fe}} f_{\text{Fe}} + \Phi_{\text{FeOH}} f_{\text{FeOH}}) I_0 (1 - 10^{-\text{Abs}_{254}}) \\ & + k_3 [\text{Fe}^{2+}] [\text{H}_2\text{O}_2] - k_4 [\cdot\text{OH}] [\text{Fe}^{2+}] - k_5 [\cdot\text{OH}] [\text{H}_2\text{O}_2] - k_{13} [\cdot\text{OH}] [\text{HO}_2\cdot] \\ & - k_{14} [\cdot\text{OH}] [\text{O}_2^{\cdot-}] - 2k_{15} [\cdot\text{OH}] [\cdot\text{OH}] - k_{16} [\cdot\text{OH}] [p\text{-cresol}] \\ & - k_{17} [4\text{MC}] [\cdot\text{OH}] - 2k_{18} [4\text{MB}] [\cdot\text{OH}] - 4k_{19} \gamma_{\pm 1} [3\text{MM}^-] [\cdot\text{OH}] \\ & - k_{20} \gamma_{\pm 1} [\text{L}^-] [\cdot\text{OH}] - k_{21} \gamma_{\pm 1} [\text{Ox}^-] [\cdot\text{OH}] - k_{22} \gamma_{\pm 2} [\text{Ox}^{2-}] [\cdot\text{OH}] \\ & - k_{24} [\text{HA}] [\cdot\text{OH}] - k_{25} \gamma_{\pm 1} [\text{A}^-] [\cdot\text{OH}] - k_{26} \gamma_{\pm 1} [\text{F}^-] [\cdot\text{OH}] \end{aligned} \quad \text{Eq (C-7)}$$

$$\begin{aligned}
\frac{d[\text{Fe}^{2+}]}{dt} = & (\Phi_{\text{Fe}}f_{\text{Fe}} + \Phi_{\text{FeOH}}f_{\text{FeOH}})I_0(1 - 10^{-\text{Abs}_{254}}) + k_1[\text{Fe}(\text{HO}_2)^{2+}] \\
& + k_2[\text{Fe}(\text{OH})(\text{HO}_2)^+] - k_3[\text{Fe}^{2+}][\text{H}_2\text{O}_2] - k_4[\text{Fe}^{2+}][\cdot\text{OH}] \\
& - k_6[\text{Fe}^{2+}][\text{HO}_2\cdot] - k_7[\text{Fe}^{2+}][\text{O}_2^{\cdot-}] + k_8[\text{HO}_2\cdot][\text{Fe}(\text{III})] \\
& + k_9[\text{O}_2^{\cdot-}][\text{Fe}(\text{III})]
\end{aligned} \tag{C-8}$$

$$\frac{d[\text{Fe}(\text{III})]_{\text{tot}}}{dt} = -\frac{d[\text{Fe}^{2+}]}{dt} \tag{C-9}$$

$$\frac{d[p\text{-cresol}]}{dt} = -\Phi_{p\text{-cresol}}f_{p\text{-cresol}}I_0(1 - 10^{-\text{Abs}_{254}}) - k_{16}[p\text{-cresol}][\cdot\text{OH}] \tag{C-10}$$

where

$$[\text{Fe}(\text{III})]_{\text{tot}} = [\text{Fe}(\text{III})] + [\text{Fe}(\text{HO}_2)^{2+}] + [\text{Fe}(\text{OH})(\text{HO}_2)^+] \tag{C-11}$$

$$[\text{Fe}(\text{III})] = [\text{Fe}^{3+}] + [\text{Fe}(\text{OH})^{2+}] + [\text{Fe}(\text{OH})_2^+] + 2[\text{Fe}_2(\text{OH})_2^{4+}] \tag{C-12}$$

$$\gamma_{\pm 1} = 10^{-0.51 \times (\pm 1)^2 \left(\frac{\sqrt{\text{ionic strength}}}{1 + \sqrt{\text{ionic strength}}} - 0.2 \times \text{ionic strength} \right)} \tag{C-13}$$

and

$$[\text{Fe}(\text{OH})^{2+}] = \frac{K_1[\text{Fe}^{3+}]}{[\text{H}^+]} \tag{C-14}$$

$$[\text{Fe}(\text{OH})_2^+] = \frac{K_2[\text{Fe}^{3+}]}{[\text{H}^+]^2} \tag{C-15}$$

$$[\text{Fe}_2(\text{OH})_2^{4+}] = \frac{K_3[\text{Fe}^{3+}]^2}{[\text{H}^+]^2} \tag{C-16}$$

$$[\text{Fe}(\text{HO}_2)^{2+}] = \frac{K_4[\text{Fe}^{3+}][\text{H}_2\text{O}_2]}{[\text{H}^+]} \quad \text{Eq (C-17)}$$

$$[\text{Fe}(\text{OH})(\text{HO}_2)^+] = \frac{K_5[\text{Fe}(\text{OH})^{2+}][\text{H}_2\text{O}_2]}{[\text{H}^+]} = \frac{K_1 K_5 [\text{Fe}^{3+}]^2 [\text{H}_2\text{O}_2]}{[\text{H}^+]^2} \quad \text{Eq (C-18)}$$

$$[\text{H}^+] = \frac{\{\text{H}^+\}}{\gamma_{\pm 1}} = \frac{10^{-\text{pH}}}{\gamma_{\pm 1}} \quad \text{Eq (C-19)}$$

Reaction rate expressions for other radicals and *p*-cresol $\cdot\text{OH}$ oxidation by-products are available in the supplementary data. The resultant set of simultaneous, ordinary differential equations/algebraic equations was solved using the MATLAB (R2016a) ode15s solver.

C.3.2 Iron Solution Speciation Prediction

At a given pH, H_2O_2 concentration, total iron and Fe(II) contents, the composition of an iron solution with 0.1 M ionic strength can be computed by solving equations Eq (C-20) - (C-22) for the three unknowns: $[\text{Fe}^{3+}]$, $[\text{ClO}_4^-]$ and $[\text{Na}^+]$. These equations are based on the iron mass balance, charge balance and solution ionic strength. They were solved using MATLAB (R2016a) fsolve.

$$\begin{aligned} [\text{Fe}]_{\text{tot}} = & [\text{Fe}^{3+}] + [\text{Fe}(\text{OH})^{2+}] + [\text{Fe}(\text{OH})_2^+] + 2[\text{Fe}_2(\text{OH})_2^{4+}] \\ & + [\text{Fe}(\text{HO}_2)^{2+}] + [\text{Fe}(\text{OH})(\text{HO}_2)^+] + [\text{Fe}^{2+}] \end{aligned} \quad \text{Eq (C-20)}$$

$$\begin{aligned} [\text{OH}^-] + [\text{ClO}_4^-] = & 3[\text{Fe}^{3+}] + 2[\text{Fe}(\text{OH})^{2+}] + [\text{Fe}(\text{OH})_2^+] + 4[\text{Fe}_2(\text{OH})_2^{4+}] \\ & + 2[\text{Fe}(\text{HO}_2)^{2+}] + [\text{Fe}(\text{OH})(\text{HO}_2)^+] + 2[\text{Fe}^{2+}] + [\text{Na}^+] \\ & + [\text{H}^+] \end{aligned} \quad \text{Eq (C-21)}$$

$$\begin{aligned}
 \text{Ionic strength} = & 0.5(16[\text{Fe}_2(\text{OH})_2^{4+}] + 9[\text{Fe}^{3+}] + 4([\text{Fe}(\text{OH})^{2+}] + [\text{Fe}(\text{HO}_2)^{2+}] \\
 & + [\text{Fe}^{2+}]) + [\text{Fe}(\text{OH})_2^+] + [\text{Fe}(\text{OH})(\text{HO}_2)^+] + [\text{Na}^+] + [\text{H}^+] \\
 & + [\text{OH}^-] + [\text{ClO}_4^-])
 \end{aligned}
 \tag{C-22}$$

The resultant pH-dependent mole fractions of primary Fe(III) species for the case in which $[\text{Fe(III)}] = 0.1 \text{ mM}$ and ionic strength is 0.1 M are as shown (Figure C-2).

Figure C-2. Computed molar fractions of individual iron species as functions of pH. Iron was added as $\text{Fe}(\text{ClO}_4)_3$ with $[\text{Fe(III)}] = 0.1 \text{ mM}$ and ionic strength = 0.1 M .

C.3.3 Absorption Spectrum Calculation

Using the calculated solution composition shown above, total absorption spectra from 200 to 380 nm were calculated using following equation:

$$\text{Abs}_\lambda = \sum \epsilon_{i-\lambda} [i] \quad \text{Eq (C-23)}$$

where $\epsilon_{i-\lambda}$ is molar absorptivity ($\text{M}^{-1}\text{cm}^{-1}$) at wavelength λ of species i , including Fe^{3+} , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}_2(\text{OH})_2^{4+}$, $\text{Fe}(\text{HO}_2)^{2+}$, $\text{Fe}(\text{OH})(\text{HO}_2)^+$, Fe^{2+} , Na^+ , ClO_4^- and H_2O_2 (Table C1-1).

C.4 Results and Discussion

In principle, the kinetic model for the photo-Fenton system should also be able to predict reactor performance for the following special cases: (i) iron solution with H_2O_2 without irradiation, i.e.—Fenton-like system and (ii) H_2O_2 aqueous solution without iron, with irradiation, i.e.— H_2O_2 direct UV_{254} photolysis. Before engaging in these experiments, the accuracies of iron species equilibria and light extinction parameters for individual species were confirmed by comparing experimentally determined absorption spectra of $\text{Fe}(\text{ClO}_4)_3$ solutions with spectra predicted using equations Eq (C-20) - (C-23) (Figure C-3).

Figure C-3. Absorption spectra of Fe(ClO₄)₃ solutions with (a) [Fe(III)] = 0.1 mM at different pH values and (b) different Fe(III) content at pH 3. Solid lines represent model predictions.

Results of both Fenton-like and H₂O₂ direct UV₂₅₄ photolysis experiments are well predicted by the kinetic model (Figure C-4), illustrating the ability of the model to simulate the iron photolysis process once relevant photochemical constants, i.e.—quantum yields of Fe³⁺ and FeOH²⁺ and molar absorptivities of light absorbing compounds—are determined.

Figure C-4. Time-dependent H_2O_2 concentrations for (a) $\text{Fe}(\text{ClO}_4)_3$ solutions with $[\text{Fe}(\text{III})]_0 = 0.1 \text{ mM}$ at pH values from 2.1-3.0 without UV_{254} irradiation and (b) different H_2O_2 aqueous solutions with UV_{254} irradiation (pH = 5.6) and without iron. Solid lines represent kinetic simulations.

Good agreement between measured and calculated spectra of iron solutions under these conditions supports the validity of solution speciation calculations, as well as the molar absorptivity data for light absorbing species, both of which are key components of the general kinetic model.

The second step of the investigation was to verify the quantum yields of Fe^{3+} and $\text{Fe}(\text{OH})^{2+}$. *p*-Cresol, whose reaction with hydroxyl radical has a rate constant of $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, was used to quench $\cdot\text{OH}$, minimizing the oxidation of $\text{Fe}(\text{II})$ to $\text{Fe}(\text{III})$. Excess *p*-cresol ($100 \text{ } \mu\text{M}$ initially) was maintained throughout the 90-second irradiation experiments so that $k_{16}[\text{p-cresol}][\cdot\text{OH}] \gg k_4[\text{Fe}^{2+}][\cdot\text{OH}]$. To generate significant spread

in resultant trajectories of free ferrous ion, $\text{Fe}(\text{ClO}_4)_3$ solutions at pH 2 and 3 were irradiated with UV light. Results are summarized in Figure C-5a. Data for control experiments without *p*-cresol as well as absence of irradiation are shown in Figure C-5b.

Figure C-5. Time-dependent $\text{Fe}(\text{II})$ trajectories in $\text{Fe}(\text{ClO}_4)_3$ solutions with $[\text{Fe}]_{\text{tot}} = [\text{Fe}(\text{III})]_0 = 0.1 \text{ mM}$ at (a) pH = 2 and 3 with *p*-cresol present and (b) pH = 3 with and without *p*-cresol, including a lamp out test (without *p*-cresol). Solid lines represent kinetic model predictions. For experiments with *p*-cresol, $[\text{p-cresol}]_0 = 100 \text{ }\mu\text{M}$. The insert shows the measured (circles) and predicted (solid line) fractional *p*-cresol residuals in the reactor at pH = 3.

$\text{Fe}(\text{II})$ accumulation in the first 30 seconds of the experiment was well predicted by the kinetic model at both pHs, which confirms the reported values of Φ_{Fe} and Φ_{FeOH} from Lee and Yoon (2004a). The formation rates of $\text{Fe}(\text{II})$ from Fe^{3+} and FeOH^{2+} photolysis were $5.24 \times 10^{-8} \text{ M/s}$ and $1.20 \times 10^{-7} \text{ M/s}$ at pH 2 and pH 3, respectively (Eq C-1). Assuming that these rates remained essentially constant and ignoring other reactions, development of $\text{Fe}(\text{II})$ after 30 seconds at pH 2 and pH 3 would be $1.6 \text{ }\mu\text{M}$ and $3.6 \text{ }\mu\text{M}$. This

approximation provides the same result as the kinetic model (Figure C-5a). In other words, with the $\cdot\text{OH}$ scavenger present, the evolution of Fe(II) was due exclusively to Fe^{3+} and FeOH^{2+} photolysis. Absent *p*-cresol, however, the Fe(II) concentration grew more slowly, especially after 30 seconds (Figure C-5b). When the UV source was eliminated, the Fe(II) concentration stopped increasing immediately and decreased slightly during the next five seconds.

After about 30 seconds of irradiation, a small deviation between data and simulation is apparent (Figure C-5a). Even after 90 seconds of the experiment, however, $k_{16}[\textit{p}\text{-cresol}] \gg k_4[\text{Fe}^{2+}]$, noting that the Fe(II) concentration was about 9 μM (data at pH 3). It is unlikely that the concentration of *p*-cresol was much affected during that period. Thus the deceleration of Fe(II) accumulation cannot be explained by our current kinetic model. Potential explanations for the discrepancy lie in (i) the reoxidation of Fe(II) by reactive intermediates other than hydroxyl radical, e.g., H_2O_2 developed through a mechanism that was not including in our model or (ii) an unanticipated reaction involving reactive intermediate(s) derived from the oxidation of *p*-cresol by $\cdot\text{OH}$.

In order to explore Fe(II) behavior over a long time scale in the presence of excess *p*-cresol, an 8-hr irradiation study including a light-out test at $t = 405$ min was carried out. Per Figure C-6, Fe(II) accumulated rapidly during the first 10 minutes, and this fast growth is well represented by the model. Beyond $t \approx 15$ min, however, the measure accumulation of Fe(II) lagged behind simulation results significantly, so that Fe(II) reached a maximum at $t = 210$ min $[\text{Fe(II)}]/[\text{Fe}]_{\text{tot}} \approx 0.7$ ratio and declined thereafter, presumably due to the gradual disappearance of the $\cdot\text{OH}$ scavenger ($[\textit{p}\text{-cresol}] < 10 \mu\text{M}$). The model, however, quickly reached steady state with $[\text{Fe(II)}]/[\text{Fe}]_{\text{tot}} \approx 1.0$ at $t = 90$ min.

Figure C-6. *p*-Cresol and Fe(II) concentrations as functions of irradiation time in $\text{Fe}(\text{ClO}_4)_3$ solution with $[\text{Fe}(\text{III})]_0 = 0.1 \text{ mM}$, $[\text{p-cresol}]_0 = 100 \text{ }\mu\text{M}$ at pH 2.4. Blue (*p*-cresol) and red (Fe(II)) solid lines represent simulations. The black solid line represents the predicted result based on the measured Fe(II) and H_2O_2 concentrations when the lamp was turned off at $t = 405 \text{ min}$.

The rapid decomposition of *p*-cresol in the first 60 minutes is due to the fast reaction between *p*-cresol and the $\cdot\text{OH}$ generated from Fe(III) photolysis, which essentially eliminated the reaction of $\cdot\text{OH}$ with Fe^{2+} . A concentration of $6 \text{ }\mu\text{M}$ of H_2O_2 was measured when the lamp was turned off at $t = 405 \text{ min}$, which is much higher than the predicted level (10^{-14} M). As a consequence, the Fe(II) level dropped from $50 \text{ }\mu\text{M}$ to $40 \text{ }\mu\text{M}$ over the next few minutes. That change was well predicted by the model (black solid line).

In total, results shown to this point indicate that the kinetic model developed here can predict the behavior of: (1) the UV/ H_2O_2 process, (2) the Fenton's reaction process, (3) the direct photolysis of *p*-cresol and H_2O_2 , and (4) Fe(III) photolysis at relatively short

times (Figure C-5). However, when the model is applied to Fe(III) photolysis in long-term experiments (Figure C-7), large discrepancies arise.

Figure C-7. Fe(II) vs. time in Fe(ClO₄)₃ solutions with (a) [Fe(III)]₀ = 0.1 mM at different pH values and (b) different initial Fe(III) concentrations at pH 3 under UV₂₅₄ irradiation. Solid lines represent kinetic model predictions.

Model deficiencies are even more apparent in long term photolysis experiments/simulations (Figure C-7). Under all experimental conditions, Fe(II) accumulated far more rapidly than predicted during the first few minutes of the experiment. The rate of increase of Fe(II) concentration decreased continuously over the hour-long experiments but remained positive throughout. Two trends are clear from the results shown: (1) At constant pH, observed rates of Fe(II) accumulation are directly related to initial Fe(III) concentrations and (2) at the same initial Fe(III) concentration, higher solution pH favors the accumulation of Fe(II). Both observations are subjectively consistent with the kinetic model proposed. Nevertheless, the most obvious result of the long-term experiments is the underprediction of time-dependent Fe(II) concentrations by the model. Measured absorption spectra in samples taken during these experiments were in excellent agreement with spectra predicted on the basis of measured Fe(II) concentrations and Fe(III) species calculated on the basis of total iron and pH measurements (Figure C-8)—eliminating the possibility of analytical error in the measurement of iron forms.

Figure C-8. Comparison of measured (red circles) and predicted (solid lines) spectra in long term photolysis experiments after (a) 0, (b) 5, (c) 20 and (d) 60 minutes.. Initial experimental conditions were as indicated in Figure C-7: $[\text{Fe}]_{\text{tot}} = [\text{Fe(III)}]_0 = 0.1 \text{ mM}$ at $\text{pH} = 3$.

By employing OriginPro 2016 (v. 9.3.2), a trendline was fitted (using B-spline connection fitting) to the experimental data on Fe(II) vs. time for the experiment with $[\text{Fe}]_{\text{tot}} = [\text{Fe(III)}]_0 = 0.1 \text{ mM}$ at $\text{pH} = 3$, in order to yield a continuous smooth curve of the overall accumulation rate of Fe(II) as a function of irradiation time. Results are presented in Figure C-9.

Figure C-9. Overall Fe(II) accumulation rates obtained from the kinetic model and experimental data versus irradiation time for the experiment with $[\text{Fe}]_{\text{tot}} = [\text{Fe(III)}]_0 = 0.1$ mM at pH = 3. The inset illustrates the trendline fitted to experimental data.

Per Figure C-9, the initial accumulation rate of Fe(II), which is determined by Eq (C-1) in model calculations, is the same for both curves. However, the model predicts a decrease in the net rate of iron reduction from 10^{-7} M/s to 10^{-9} M/s within in the first minute of the experiment, while the observed accumulation rate decreased much more slowly. After the first few minutes, both model and data follow similar trends (i.e., the fractional difference between observed and measured rates of Fe(II) accumulation remain essentially constant). The failure of the model to reproduce the long-term experiments is apparently due to inaccuracies at the start of the process.

Based on the proposed reaction mechanism (Table C-1), six elementary reactions (P1, P2, R1, R2, R8 and R9) produce Fe(II), and four (R3, R4, R6 and R7) oxidize Fe(II). The

(predicted) individual contribution of each elementary reaction to the net rate of Fe(II) accumulation over the hour-long experiments was as shown (Figure C-10). Initial conditions for the exercise were as follows: $[\text{Fe}]_{\text{tot}} = [\text{Fe(III)}]_0 = 0.1 \text{ mM}$ at $\text{pH} = 3$.

Figure C-10. Contributions of elementary reactions (Table C-1) to the production (a) and consumption (b) of Fe(II) as a function of time during the photolysis of Fe(III)-hydroxo species. $[\text{Fe}]_{\text{tot}} = [\text{Fe(III)}]_0 = 0.1 \text{ mM}$ at $\text{pH} = 3$.

The predicted rate of formation of Fe(II) is dominated by Fe^{3+} and FeOH^{2+} photolysis throughout the experiment period. This is logical since Fe(II) remains a small fraction of total iron in the simulations. The predicted rate of Fe(II) oxidation is dominated by the reaction between Fe^{2+} and $\cdot\text{OH}$. Since the photochemical properties of Fe^{3+} and FeOH^{2+} have been validated, it is likely that the kinetic model overestimates the oxidation rate of Fe(II) by $\cdot\text{OH}$ in the first minute, suggesting that hydroxyl radical does not increase as rapidly as predicted by the model or that the reaction of Fe(II) with hydroxyl radical is much slower than was originally estimated. Possibilities include that either (i) something

in the reactor quenches $\cdot\text{OH}$ at the start of the experiment, or (ii) Fe(II) was somehow “shielded”, inhibiting oxidation of Fe(II) by $\cdot\text{OH}$. Results generated in the presence of excess *p*-cresol (Figure C-5b) clearly show that the fault in the model does not lie on the photolysis (generation) side of the Fe(II) production equation (Eq C-1).

Underestimation of Fe(II) accumulation during Fe(III) photolysis was noted previously. Wang and Liu (2014) fitted experimental data under conditions similar to this work by decreasing the reaction rate constant for the oxidation of Fe^{2+} by hydroxyl radical from $3.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ to $3.47 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$. This is not supported by the work of Stuglik and Zagórski (1981), who established the higher rate constant (used here) by pulse radiolysis. The higher value is similar to that of Jayson et al. (1972) ($2.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) estimated using the same method.

The kinetic model developed here accurately predicts rates of decomposition of H_2O_2 in the Fenton system (Figure C-4a) and the H_2O_2 UV photolysis system (Figure C-4b). In addition, the simulated destructions of trace organics using the two systems are accurate, suggesting that hydroxyl radical concentrations derived from the model are also accurate (Rojas et al. 2010; 2011). The model fails, however, to predict iron behavior during Fe(III) photolysis.

To further diagnose the problem, we carried out additional Fe(III) photolysis experiments, increasing the initial concentration of H_2O_2 in a series of steps. This was designed to gradually shift the process from a predominantly photolytic system to a predominantly Fenton-driven system (Figure C-11). Deviation between experimental and predicted Fe(II) concentration profiles was much reduced at higher initial H_2O_2

concentrations. The data show that Fe(II) is initially generated faster in the reactor with 50 μM H_2O_2 compared to the H_2O_2 -free control. This is due to $\cdot\text{OH}$ quenching by H_2O_2 , which encourages Fe(II) to accumulate. However, the rate of increase of Fe(II) concentration becomes slower in the reactors with 1.0 and 12 mM H_2O_2 (initial concentrations) presumably because Fe(II) formed is reoxidized to Fe(III) by H_2O_2 , particularly in the first 5 minutes of the experiment. The trajectory of Fe(II) concentration in the reactor with 12 mM H_2O_2 exhibited three stages: (1) 0 – 5 minutes, fast buildup, (2) 5 – 30 minutes, slow and steady accumulation, and (3) 30 – 60 minutes, steadily increasing rate of accumulation (Figure C-11a). Interestingly, all three phases were predicted by the model. In addition, roughly 80% H_2O_2 loss was measured in each experiment, regardless of initial peroxide dose (Figure C-11b). Except for the H_2O_2 -free experiments, the evolution of Fe(II) is well represented by the model during the first 5 minutes. However, in the $[\text{H}_2\text{O}_2]_0 = 50 \mu\text{M}$ experiment, the predicted Fe(II) concentration reached a steady, maximum after five minutes that was not observed among the measured values. Predicted Fe(II) concentrations for the reactor with 1 mM H_2O_2 matched experimental results for the first 30 minutes before approaching a steady maximum that, again, was not observed in the data. The model accurately predicted the Fe(II) concentration throughout the 60-minute experiment at the highest initial H_2O_2 dose provided (12 mM).

Figure C-11. Measured and predicted Fe(II) concentrations (left) and H₂O₂ (right) vs. irradiation time in Fe(ClO₄)₃ solutions $[\text{Fe}]_{\text{tot}} = [\text{Fe(III)}]_0 = 0.1 \text{ mM}$ and pH = 3 under UV₂₅₄ irradiation with different initial H₂O₂ concentrations: 0 mM (∇), 0.05 mM (Δ), 1 mM ($\circ$) and 12 mM ($\square$).

To further explore inadequacies of the proposed iron conversion mechanism, experiments and simulations were carried out for Fenton and photo-Fenton systems starting with iron present as Fe(II) (Figure C-12). Absent irradiation (i.e.—Fenton system), the Fe(II) concentration dropped > 50% during the first 5 seconds of the experiment and another 25% (based on initial concentration) during the next 45 seconds. With irradiation, oxidation of Fe(II) was even faster. The model accurately predicted the decrease in Fe(II) during the Fenton experiment. Model results were unchanged by UV irradiance, whereas UV light accelerated the observed conversion of Fe(II) in the photo-Fenton experiment.

Figure C-12. Measured and predicted Fe(II) concentration versus time for Fenton and photo-Fenton experiments with $[\text{Fe}]_{\text{tot}} = [\text{Fe(II)}]_0 = 1.9 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 1 \text{ mM}$ at $\text{pH} = 2.4$.

The kinetic model was also tested for an photo-Fenton experiment that started with a Fe(II)/Fe(III) that was roughly equal to 1.0 and $\text{pH}_0 = 3.0$. The solution was UV irradiated for 30 minutes before $25 \text{ } \mu\text{M}$ H_2O_2 was spiked into the reactor. A second identical peroxide spike was added at 75 minutes total irradiation time. Fe(II) and H_2O_2 were monitored semi-continuously. The Fe(II) level was stable throughout the first 30 minutes of the experiment (Figure C-13). Following the first addition of H_2O_2 , Fe(II) was oxidized from $57 \text{ } \mu\text{M}$ to $20 \text{ } \mu\text{M}$ within 20 minutes, stabilizing around $19 \text{ } \mu\text{M}$ as peroxide was exhausted. The Fe(II) concentration decreased further, to $12 \text{ } \mu\text{M}$, and again leveled off after exhaustion of the second H_2O_2 spike. Observed characteristics in the trajectories of both Fe(II) and H_2O_2 concentrations were well described by the kinetic model.

Figure C-13. Comparison between experimental (open circles) and predicted (solid lines) Fe(II) and H_2O_2 concentrations during the photoFenton oxidation of Fe(II). Experimental conditions: $[\text{Fe}]_{\text{tot}} = 0.108 \text{ mM}$, $[\text{Fe(II)}]_0 = 57 \text{ }\mu\text{M}$, $\text{pH} = 3$. The reactor was spiked with $25 \text{ }\mu\text{M}$ H_2O_2 at $t = 30$ and 75 mins.

C.5 Conclusions

An Fe(III) UV_{254} photolysis kinetic model that combines the Fenton-like mechanism with photolysis of Fe^{3+} , FeOH^{2+} and H_2O_2 was capable of simulating the time-dependent concentrations of iron species and peroxide during direct photolysis of iron species or H_2O_2 by UV_{254} . The model accurately described solute trajectories during Fenton-like reactions. Iron speciation, Fe(III) equilibrium constants, and molar absorptivity of light absorbing compounds were validated using spectrophotometric data and published Fe(III) spectra. The validities of reported quantum yields (Φ_{Fe} and Φ_{FeOH}) were verified via irradiation experiments using excess *p*-cresol as $\cdot\text{OH}$ scavenger.

The model failed, however, to correctly represent the trajectory of iron reduction in Once $\text{Fe}(\text{ClO}_4)_3$ solutions under UV_{254} irradiation. Although model and experiment were initially in agreement, after a few minutes predicted Fe^{2+} concentrations were much lower than observations. The source of these discrepancies remains unresolved. Modeling suggests that absent addition of a hydroxide radical scavenger such as *p*-cresol, rates of iron reduction and oxidation should come into balance after a few minutes. At that point, reductions are dominated by the photolysis of $\text{Fe}(\text{III})$ -hydroxo species, and the major pathway for $\text{Fe}(\text{II})$ oxidation is the reaction of Fe^{2+} with $\cdot\text{OH}$. Overestimation of Fe^{2+} oxidation by $\cdot\text{OH}$ could arise from either (i) production of an unidentified species that reacts with hydroxyl radicals or (ii) $\text{Fe}(\text{II})$ was somehow “shielded” from reaction with $\cdot\text{OH}$ in the first few minutes of the process.

Simulations were accurate when $\text{Fe}(\text{II})$ and H_2O_2 were both initially present in the reactor (photo-Fenton model) at relatively high concentrations and when both $\text{Fe}(\text{III})$ and $\text{Fe}(\text{II})$ were initially provided at high concentrations (photolysis model).

C.6 References

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APPENDIX C1: Supplementary Materials for APPENDIX C

Reaction rate expressions of $\text{HO}_2^\bullet$, $\text{O}_2^{\bullet-}$ and 4MC along with other *p*-cresol $^\bullet\text{OH}$ oxidation intermediates that were solved for the kinetic model described in the manuscript are listed below.

$$\begin{aligned} \frac{d[\text{HO}_2^\bullet]}{dt} = & k_1[\text{Fe}(\text{HO}_2)^{2+}] + k_2[\text{Fe}(\text{OH})(\text{HO}_2)^+] + k_5[^\bullet\text{OH}][\text{H}_2\text{O}_2] - k_6[\text{HO}_2^\bullet][\text{Fe}^{2+}] \\ & - k_8[\text{HO}_2^\bullet][\text{Fe}(\text{III})] - k_{10}[\text{HO}_2^\bullet] + k_{10r}[\text{O}_2^{\bullet-}][\text{H}^+] - 2k_{11}[\text{HO}_2^\bullet][\text{HO}_2^\bullet] \\ & - k_{12}[\text{HO}_2^\bullet][\text{O}_2^{\bullet-}] - k_{13}[\text{HO}_2^\bullet][^\bullet\text{OH}] \end{aligned} \quad \text{Eq (C1-1)}$$

$$\begin{aligned} \frac{d[\text{O}_2^{\bullet-}]}{dt} = & -k_7[\text{O}_2^{\bullet-}][\text{Fe}^{2+}] - k_9[\text{O}_2^{\bullet-}][\text{Fe}(\text{III})] + k_{10}[\text{HO}_2^\bullet] - k_{10r}[\text{O}_2^{\bullet-}][\text{H}^+] \\ & - k_{12}[\text{O}_2^{\bullet-}][\text{HO}_2^\bullet] - k_{14}[\text{O}_2^{\bullet-}][^\bullet\text{OH}] \end{aligned} \quad \text{Eq (C1-2)}$$

$$\frac{d[4\text{MC}]}{dt} = -\Phi_{4\text{MC}}f_{4\text{MC}}I_o(1 - e^{-2.303A}) + k_{16}[\text{PC}][^\bullet\text{OH}] - k_{17}[4\text{MC}][^\bullet\text{OH}] \quad \text{Eq (C1-3)}$$

$$\frac{d[4\text{MB}]}{dt} = k_{17}[4\text{MC}][^\bullet\text{OH}] - k_{18}[4\text{MB}][^\bullet\text{OH}] \quad \text{Eq (C1-4)}$$

$$\frac{d[3\text{MM}^-]}{dt} = k_{18}[4\text{MB}][^\bullet\text{OH}] - k_{19}\gamma_{\pm 1}[3\text{MM}^-][^\bullet\text{OH}] \quad \text{Eq (C1-5)}$$

$$\frac{d[\text{L}^-]}{dt} = k_{19}\gamma_{\pm 1}[3\text{MM}^-][^\bullet\text{OH}] - k_{20}\gamma_{\pm 1}[\text{L}^-][^\bullet\text{OH}] \quad \text{Eq (C1-6)}$$

$$\begin{aligned} \frac{d[\text{TotOx}]}{dt} = & 2k_{19}\gamma_{\pm 1}[3\text{MM}^-][^\bullet\text{OH}] - k_{21}\gamma_{\pm 1}[\text{Ox}^-][^\bullet\text{OH}] - k_{22}\gamma_{\pm 2}[\text{Ox}^{2-}][^\bullet\text{OH}] \\ & + k_{23}\gamma_{\pm 1}[\text{Ox}^{\bullet-}]\gamma_{\pm 1}[\text{Ox}^{\bullet-}] \end{aligned} \quad \text{Eq (C1-7)}$$

$$\begin{aligned} \frac{d[\text{Ox}^{\bullet-}]}{dt} &= k_{21}\gamma_{\pm 1}[\text{Ox}^-][\cdot\text{OH}] + k_{22}\gamma_{\pm 2}[\text{Ox}^{2-}][\cdot\text{OH}] \\ &\quad - k_{23}\gamma_{\pm 1}[\text{Ox}^{\bullet-}]\gamma_{\pm 1}[\text{Ox}^{\bullet-}] \end{aligned} \quad \text{Eq (C1-8)}$$

$$\frac{d[\text{TotA}]}{dt} = k_{20}\gamma_{\pm 1}[\text{L}^-][\cdot\text{OH}] - k_{24}[\text{HA}][\cdot\text{OH}] - k_{25}\gamma_{\pm 1}[\text{A}^-][\cdot\text{OH}] \quad \text{Eq (C1-9)}$$

$$\frac{d[\text{F}^-]}{dt} = k_{24}[\text{HA}][\cdot\text{OH}] + k_{25}\gamma_{\pm 1}[\text{A}^-][\cdot\text{OH}] - k_{26}\gamma_{\pm 1}[\text{F}^-][\cdot\text{OH}] \quad \text{Eq (C1-10)}$$

$$\gamma_{\pm 1}[\text{Ox}^-] = \frac{[\text{TotOx}]}{\left\{1 + \frac{K_6}{\gamma_{\pm 1}[\text{H}^+]}\right\}} \quad \text{Eq (C1-11)}$$

$$\gamma_{\pm 2}[\text{Ox}^{2-}] = \frac{K_6\gamma_{\pm 1}[\text{Ox}^-]}{\gamma_{\pm 1}[\text{H}^+]} \quad \text{Eq (C1-12)}$$

$$[\text{HA}] = \frac{[\text{TotA}]}{\left\{1 + \frac{K_7}{\gamma_{\pm 1}[\text{H}^+]}\right\}} \quad \text{Eq (C1-13)}$$

$$\gamma_{\pm 1}[\text{A}^-] = \frac{K_7[\text{HA}]}{\gamma_{\pm 1}[\text{H}^+]} \quad \text{Eq (C1-14)}$$

where

$$\gamma_{\pm 2} = 10^{-0.51 \times (\pm 2)^2 \left(\frac{\sqrt{\text{ionic strength}}}{1 + \sqrt{\text{ionic strength}}} - 0.2 \times \text{ionic strength} \right)} \quad \text{Eq (C1-15)}$$

Table C1-1. Molar absorptivities of light-absorbing species.

Wavelength nm	Molar Absorptivity ($\text{M}^{-1}\text{cm}^{-1}$)					
	Fe^{3+}	FeOH^{2+}	$\text{Fe}(\text{OH})_2^+$	$\text{Fe}_2(\text{OH})_2^{4+}$	$\text{Fe}(\text{HO}_2)^{2+}$	$\text{Fe}(\text{OH})(\text{HO}_2)^+$
200	4.03E+03	4.72E+03	6.50E+03	3.90E+04	3.55E+03	1.18E+04
205	3.75E+03	4.87E+03	6.30E+03	3.70E+04	3.40E+03	1.17E+04
210	3.57E+03	4.82E+03	5.85E+03	3.50E+04	3.25E+03	1.16E+04
215	3.58E+03	4.51E+03	5.30E+03	3.30E+04	3.10E+03	1.15E+04
220	3.65E+03	4.10E+03	4.65E+03	3.10E+04	2.95E+03	1.14E+04
225	3.84E+03	3.40E+03	3.88E+03	2.90E+04	2.80E+03	1.13E+04
230	4.04E+03	2.80E+03	3.01E+03	2.70E+04	2.65E+03	1.12E+04
235	4.20E+03	2.25E+03	2.40E+03	2.50E+04	2.50E+03	1.11E+04
240	4.23E+03	1.75E+03	2.00E+03	2.30E+04	2.35E+03	1.10E+04
245	4.18E+03	1.39E+03	1.62E+03	2.10E+04	2.20E+03	1.09E+04
250	3.95E+03	1.15E+03	1.37E+03	1.90E+04	2.05E+03	1.08E+04
254	3.54E+03	1.06E+03	1.28E+03	1.74E+04	1.93E+03	1.07E+04
255	3.41E+03	1.05E+03	1.26E+03	1.70E+04	1.90E+03	1.07E+04
260	2.90E+03	1.06E+03	1.22E+03	1.50E+04	1.75E+03	1.06E+04
265	2.30E+03	1.11E+03	1.26E+03	1.30E+04	1.60E+03	1.05E+04
270	1.78E+03	1.29E+03	1.34E+03	1.10E+04	1.45E+03	1.04E+04
275	1.21E+03	1.56E+03	1.43E+03	9.00E+03	1.30E+03	1.03E+04
280	9.00E+02	1.82E+03	1.54E+03	7.00E+03	1.15E+03	1.02E+04
285	6.40E+02	2.00E+03	1.64E+03	5.00E+03	1.00E+03	1.01E+04
290	4.70E+02	2.07E+03	1.73E+03	3.07E+03	8.50E+02	1.00E+04
295	3.10E+02	2.10E+03	1.77E+03	2.38E+03	7.00E+02	9.90E+03
300	2.10E+02	2.09E+03	1.76E+03	2.05E+03	6.00E+02	9.80E+03
305	1.50E+02	2.04E+03	1.70E+03	2.02E+03	5.65E+02	9.08E+03
310	9.00E+01	1.95E+03	1.61E+03	2.30E+03	5.28E+02	8.35E+03
315	7.50E+01	1.82E+03	1.46E+03	3.00E+03	4.92E+02	7.63E+03
320	5.00E+01	1.67E+03	1.29E+03	3.60E+03	4.70E+02	6.90E+03
325	2.50E+01	1.49E+03	1.14E+03	4.20E+03	4.52E+02	6.18E+03
330	1.50E+01	1.30E+03	1.00E+03	4.90E+03	4.40E+02	5.45E+03
335	1.00E+01	1.15E+03	8.90E+02	5.12E+03	4.29E+02	4.73E+03
340	5.00E+00	1.00E+03	7.60E+02	5.10E+03	4.19E+02	4.00E+03
345	0.00E+00	8.40E+02	6.80E+02	4.86E+03	4.10E+02	3.30E+03
350	0.00E+00	6.90E+02	6.15E+02	4.25E+03	4.00E+02	2.60E+03
355	0.00E+00	5.50E+02	5.70E+02	3.20E+03	3.90E+02	2.30E+03
360	0.00E+00	4.00E+02	5.35E+02	2.30E+03	3.80E+02	2.00E+03
365	0.00E+00	3.20E+02	5.00E+02	1.60E+03	3.65E+02	1.75E+03
370	0.00E+00	2.10E+02	4.80E+02	1.34E+03	3.50E+02	1.50E+03
375	0.00E+00	1.65E+02	4.65E+02	1.15E+03	3.45E+02	1.30E+03
380	0.00E+00	1.20E+02	4.55E+02	1.07E+03	3.42E+02	1.10E+03

Note: Molar absorptivity information for Fe^{3+} , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}_2(\text{OH})_2^{4+}$ was obtained from Knight and Sylva (1975), $\text{Fe}(\text{HO}_2)^{2+}$, $\text{Fe}(\text{OH})(\text{HO}_2)^+$ were obtained from Gallard et al. (1999). For $\text{Fe}(\text{OH})_2^+$, $\text{Fe}_2(\text{OH})_2^{4+}$, $\text{Fe}(\text{HO}_2)^{2+}$ and $\text{Fe}(\text{OH})(\text{HO}_2)^+$, molar absorptivity below 215 nm, 285 nm, 290 nm and 290 nm, respectively, were linearly extrapolated from literature values at higher wavelengths.

Table C1-1. (Continued)

Wavelength nm	Molar Absorptivity ($M^{-1}cm^{-1}$)				
	Fe^{2+}	ClO_4^-	Na^+	H_2O_2	<i>p</i> -cresol
200	3.04E-01	4.65E+01	1.44E-01	1.57E+02	1.39E+04
205	2.34E-01	3.21E+01	7.45E-02	1.50E+02	6.01E+03
210	1.78E-01	2.66E+01	5.45E-02	1.32E+02	5.70E+03
215	1.39E-01	2.84E+01	4.50E-02	1.14E+02	6.01E+03
220	8.10E-02	3.03E+01	4.45E-02	9.62E+01	6.23E+03
225	3.54E-02	3.20E+01	3.27E-02	7.81E+01	5.16E+03
230	2.53E-02	3.34E+01	2.67E-02	6.33E+01	2.51E+03
235	1.02E-02	3.41E+01	1.83E-02	5.00E+01	7.60E+02
240	5.10E-03	3.35E+01	1.28E-02	3.91E+01	2.80E+02
245	1.05E-03	3.29E+01	9.66E-03	3.05E+01	1.90E+02
250	1.00E-04	2.95E+01	9.16E-03	2.33E+01	2.35E+02
254	1.00E-04	2.67E+01	9.30E-03	1.87E+01	3.40E+02
255	1.00E-04	2.60E+01	9.33E-03	1.75E+01	3.70E+02
260	1.00E-04	1.92E+01	1.12E-02	1.34E+01	6.25E+02
265	1.00E-04	1.37E+01	1.07E-02	9.80E+00	9.70E+02
270	1.00E-04	8.95E+00	1.07E-02	7.26E+00	1.42E+03
275	1.00E-04	5.72E+00	9.83E-03	5.36E+00	1.74E+03
280	1.00E-04	3.67E+00	8.83E-03	3.91E+00	1.68E+03
285	1.00E-04	3.35E+00	6.16E-03	3.09E+00	1.30E+03
290	1.00E-04	1.48E+00	3.50E-03	2.12E+00	4.25E+02
295	1.00E-04	1.48E+00	1.67E-03	1.76E+00	8.00E+01
300	1.00E-04	1.33E+00	3.33E-04	1.00E+00	6.50E+01
305	1.00E-04	1.33E+00	2.22E-04	6.50E-01	3.75E+01
310	1.00E-04	1.33E+00	2.05E-04	4.50E-01	3.00E+01
315	1.00E-04	1.33E+00	1.85E-04	3.00E-01	2.00E+01
320	1.00E-04	1.33E+00	1.67E-04	2.20E-01	1.75E+01
325	1.00E-04	8.28E-01	1.17E-03	1.50E-01	7.50E+00
330	1.00E-04	8.28E-01	1.83E-03	1.00E-01	5.00E+00
335	1.00E-04	8.28E-01	2.83E-03	7.00E-02	2.50E+00
340	1.00E-04	8.28E-01	3.33E-03	4.50E-02	2.50E+00
345	1.00E-04	8.28E-01	3.00E-03	3.50E-02	2.50E+00
350	1.00E-04	5.05E-01	3.50E-03	2.40E-02	2.50E+00
355	1.00E-04	5.05E-01	3.50E-03	1.50E-02	1.00E+00
360	1.00E-04	5.05E-01	4.00E-03	1.00E-02	5.00E-01
365	1.00E-04	5.05E-01	3.17E-03	8.00E-03	1.00E-01
370	1.00E-04	5.05E-01	3.17E-03	5.00E-03	5.00E-02
375	1.00E-04	5.05E-01	3.17E-03	3.50E-03	1.00E-02
380	1.00E-04	5.05E-01	3.67E-03	2.40E-03	5.00E-03

Note: Data for Fe^{2+} , ClO_4^- , Na^+ , H_2O_2 and *p*-cresol were experimentally determined in this study.

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**APPENDIX D: Modeling the Oxidation of Phenolic Compounds by Hydrogen
Peroxide Photolysis**

This article was published in Chemosphere (2016)

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Abstract

Hydrogen peroxide UV photolysis is among the most widely used advanced oxidation processes (AOPs) for the destruction of trace organics in waters destined for reuse. Previous kinetic models of hydrogen peroxide photolysis focus on the dynamics of hydroxyl radical production and consumption, as well as the reaction of the target organic with hydroxyl radicals. However, the rate of target destruction may also be affected by radical scavenging by reaction products. In this work, we build a predictive kinetic model for the destruction of *p*-cresol by hydrogen peroxide photolysis based on a complete reaction mechanism that includes reactions of intermediates with hydroxyl radicals. The results show that development of a predictive kinetic model to evaluate process performance requires consideration of the complete reaction mechanism, including reactions of intermediates with hydroxyl radicals.

D.1 Introduction

Alkylphenol ethoxylates are non-ionic surfactants commonly used to formulate products such as detergents, paints, dispersing agents, wetting products, pesticides, and lubricants (Nagarnaik and Boulanger 2011). These compounds are converted into alkylphenols in bioreactors used in wastewater treatment (Ahel et al. 1996), leading to their presence in surface waters (Scullion et al. 1996; Dong et al. 2015), groundwater (Swartz et al. 2006), municipal and industrial wastewater (Loyo-Rosales et al. 2007), aquatic sediments and marine shellfish (Lye et al. 1999). The most commonly detected metabolite, *p*-nonylphenol, induces breast tumor cell proliferation (Soto et al. 1991) and is a recognized endocrine disrupter (Lee and Lee 1996). Therefore, the fates of *p*-nonylphenol and other phenolic compounds during wastewater treatment and following the release of treated wastewater into the environment is of practical importance.

Advanced oxidation processes (AOPs) are effective treatments for phenolic compounds due to their high rates of reaction with hydroxyl radicals (second-order rate constants in the range 10^9 — 10^{10} $\text{M}^{-1}\text{s}^{-1}$; Buxton et al. 1988). The UV photolysis of hydrogen peroxide (UV/H₂O₂) is among the most widely used AOPs in water treatment. Various models have been developed to simulate process kinetics. Common elements in these models include: (i) the kinetics of radical production from the direct photolysis of hydrogen peroxide, and hydroxyl radical scavenging by hydrogen peroxide and other radicals; (ii) reaction of hydroxyl radicals with the target compound and, although to a lesser extent, (iii) radical scavenging by reaction byproducts and intermediates (Lay 1989; Glaze et al. 1995; Liao and Gurol 1995; Stefan et al. 1996; Crittenden et al. 1999; Murcia et al. 2015; Rojas et al. 2010, 2011).

The first step in the reaction mechanism for radical oxidation of phenolic compounds is OH addition to the ring (Wojnárovits et al. 2002). The position of OH addition is controlled by substitutions on the ring, but *para*- and *ortho*-hydroxylation normally predominate due to the electrophilic nature of the hydroxyl radical (Omura and Matsuura 1968; Matsuura and Omura 1974). Further oxidation of the resulting dihydroxy compound occurs via abstraction of a hydrogen atom to form benzoquinones, after which the ring can be cleaved to yield aliphatic acids (Scheck and Frimmel 1995).

Previous efforts on the kinetic modeling of the UV/H₂O₂ process generally include a complete description of the chemistry behind radical formation, but rarely consider reaction intermediate and byproducts. Glaze et al. (1995) proposed a kinetic model containing the most important elements of UV/H₂O₂ photolysis to predict the time-dependent concentration of a halogenated target. They used a quasi-steady-state assumption (QSSA) to calculate the time-dependent concentrations of free radicals. Their model did not account for CO₂ evolution/pH change and neglected the role of all radical scavenging species except H₂O₂. Stefan et al. (1996) followed a similar approach, but assumed that the target compound (in their case acetone) was transformed to oxalic and formic acids and then to CO₂. Subsequently, Crittenden et al. (1999) modeled UV/H₂O₂ process without reliance on a quasi-steady-state assumption for radical concentrations. Their work showed that the QSSA tends to under-predict hydroxyl radical concentrations in some cases and therefore the rates of target compound decomposition. Furthermore, their model included radical scavenging reactions.

The model of Song et al. (2008) accounted for time-dependent radical concentrations, pH changes due to product formation (CO_2 and low molecular weight acids), and radical scavenging by H_2O_2 and natural organic matter.

More recent modeling efforts of oxidation of phenolic compounds usually include a full formulation of the dynamics of radical formation, but very few or no details of the influence of intermediate compounds and by-products over target compound degradation. De Luis et al. (2011) presented a model of phenol and cresol degradation during the UV/ H_2O_2 process that considered possible reactions of the organic compounds with produced radicals, but without considering intermediate compounds and by-products. A similar approach was followed by Rojas et al. (2010, 2011) to model the UV/ H_2O_2 and Fenton's reaction processes. Moreira et al. (2012) developed a phenomenological model to simulate the TiO_2 photocatalysis of phenol, which includes specific details about the reaction mechanism.

In this work, *p*-cresol was selected as an example of a substituted phenolic compound. Even though *p*-cresol itself is not a common trace organic in wastewater effluent, it has chemical structure and reactivity with hydroxyl radicals similar to *p*-nonylphenol, which is a common endocrine disrupter compound widely present in wastewater effluent. A mechanism for radical-dependent UV/photolysis was proposed and calibrated based on time-dependent measurements of *p*-cresol and a number of reaction products/intermediates in a batch reactor. The model accounts for changes in ionic strength and pH due to reactant conversions. Reactor fluence rate and the *p*-cresol quantum yield during direct photolysis were considered in the kinetic model. The

calibrated model was employed to predict the evolution of concentrations of *p*-cresol and reaction intermediates under various experimental conditions.

D.2 Materials and Methods

D.2.1 Chemicals

All chemicals were obtained from commercial sources and used without further purification, including *p*-cresol (Acros, 99+%), 4-methylcatechol (Acros, 98%), hydrogen peroxide (Acros, 50 wt%), titanium sulfate (Pfaltz&Bauer, 30%), formate (Fluka, 1000 mg/L $\pm$ 4 mg/L), acetate (Fluka, 1000 mg/L $\pm$ 4 mg/L), oxalate (Fluka, 1000 mg/L $\pm$ 4 mg/L), and TOC standard (Fluka, 50 mg/L $\pm$ 2 mg/L). Methanol (Fisher Chemical, HPLC Grade) and acetonitrile (Fisher Chemical, HPLC Grade) were solvents for HPLC analyses. Milli-Q water (resistivity $\geq 18.0 \text{ m}\Omega \text{ cm}^{-1}$) was obtained from a Barnstead NANOpure II system. Glassware was washed and heated overnight at 550 °C prior to use.

D.2.2 Experimental Procedure

All experiments were conducted in a cylindrical (14-cm diameter, 950-mL) glass batch reactor, equipped with low pressure (LP) UV lamp, UV fluence meter (Hamamatsu, H8025-254) and magnetic stirrer. Stock solutions of *p*-cresol were prepared one day before use. 4-Methylcatechol stock solutions were prepared a half hour before use in amber glass containers. The UV lamp (43-cm long) was turned on two hours before the experiments. The lamp position was 21 cm above the liquid level in the reactor. A quartz sleeve covered the lamp to cut-off wavelengths below 185 nm. Solution volume was 300 mL in all experiments (liquid depth was 1.95 cm). Experiments were initiated by

exposing the reactor to UV light. Experiment duration depended on the initial *p*-cresol concentration but ranged from one to three hours. Samples were analyzed immediately after withdrawal. Dilution was frequently necessary to maintain concentrations within the recommended analytical range. Temperature was maintained at $T = 24.5 \pm 0.5$ °C. The trajectory of solution pH was determined in each experiment.

D.2.3 Analysis

The concentration of *p*-cresol was measured by fluorescence spectrometry (PerkinElmer LS 55). The inner filter effect (IFE) caused by light absorption and reabsorption of light-absorbing compounds was corrected mathematically, accounting for the absorption spectrum of the sample (MacDonald et al., 1997). Solution spectra were measured using an UV—Vis spectrophotometer (Thermo Science, Genesys 10s). Even though the reaction intermediate 4-methylcatechol is produced in concentrations that are comparable in order of magnitude to *p*-cresol, independent measurements showed that its fluorescence intensities were negligible compared to those of *p*-cresol in the relevant range of wavelengths.

Analysis of primary intermediates, particularly 4-methylcatechol, was carried out by HPLC (Agilent Technologies, 1200 Series) with a Polar-RP, 80 A column (15 cm × 4.6 mm × 4 mm) (Phenomenex) and UV/VIS detector at 280 nm. Elution solvents were 10% methanol in water (A) and acetonitrile (B), $Q = 0.4$ mL/min. The mobile phase initially consisted of 45% vol. B, linearly ramped to 65% vol. B at 15 min and then restored to the initial condition.

Formate, acetate and oxalate were measured via ion chromatography (Dionex, ICS-5000) equipped with an AS18 column (2×250 mm) (Dionex IonPac™), an AG18 guard column (2×50 mm) (Dionex IonPac™), and an AS-DV (Dionex) autosampler. Ions were detected by suppressed conductivity of the eluent using an ASRS-2mm self-regenerating suppressor (Dionex). The eluent (KOH solution; $Q = 0.4$ mL/min) was programmed as follows: 1 mM for 8 min, ramped (linearly) to 30 mM in 20 min, then immediately restored to 1 mM.

Hydrogen peroxide was measured using a modified peroxytitanic (colorimetric) method (Boltz and Holwell 1978). Absorbance was measured spectrophotometrically (Thermo Science, Genesys 10s) at 407 nm. Samples were diluted to maintain absorbance values within linear limits. TOC was monitored using a Total Organic Carbon analyzer (Shimadzu, TOC-V_{CSH}).

D.2.4 Proposed Mechanism

The proposed mechanism of *p*-cresol oxidation by hydroxyl radicals is shown in Figure D-1. The first step is OH radical addition to the ring to form 4-methylcatechol (Matsuura and Omura 1974; Olariu et al. 2002). Two possible pathways (Omura and Matsuura 1968; Scheck and Frimmel 1995) are used to explain the hydroxylation. One is the attack of OH radical on the phenolic ring, resulting in the formation of a cyclohexadienyl radical, which is subsequently converted into 4-methylcatechol. The other involves abstraction of a hydrogen atom yielding a phenoxyl radical that can combine with a second OH radical. However, the hydrogen abstraction reaction of a methyl H atom (Wang et al. 1998) is at least one order of magnitude slower than the formation of a

cyclohexadienyl radical (Sehested et al. 1975; Wojnárovits et al. 2002). Further hydroxylation may convert 4-methylcatechol; however, this reaction has negligible yield (Scheck and Frimmel 1995). Oxidation of 4-methylcatechol to 4-methylbenzoquinone occurs in two steps: the OH radical attacks the ring forming a 4-methylcatechol semiquinone radical (Gohn and Getoff 1977), after which the semiquinone radical converts to 4-methylbenzoquinone in the presence of molecular oxygen (Davies et al. 1995). Once 4-methylbenzoquinone is formed, ring tension and oxidizing agents force fission of the ring. The C—C bond in the ring between the carbons attached to oxygen atoms is cleaved, and 3-methyl-muconic acid is one of the fission products (Pospisil et al. 1957; Scheck and Frimmel 1995). Oxidation of 3-methyl-muconic acid involves the carbon double bonds. Because of the higher acidity of the α -hydrogen adjacent to the double bond, it can be easily abstracted by the OH radical (Jin et al. 2010; Huang et al. 2011). Low molecular weight organic acids such as lactic and oxalic acid are oxidation products. The abstraction of α -hydrogen next to a —COOH group by OH radical forms additional low-molecular -weight acids such as acetic and formic acids (Boonrattanakij et al. 2009). Eventually, oxalic acid, acetic acid and formic acid are oxidized by OH radicals to carbon dioxide (Getoff et al. 1971; Leitner and Dore 1997; Hart 1951; Sun and Saeys 2008).

Figure D-1. Proposed mechanism of *p*-cresol oxidation by hydroxyl radicals (see text for description).

D.2.5 Kinetic Model

The proposed kinetic model for the oxidation of *p*-cresol during UV/H₂O₂ photolysis consists of 36 reactions (Table D-1). The UV/H₂O₂ photolysis mechanism, including an initiation step that produces hydroxyl radical ([•]OH) and propagation steps that scavenge [•]OH and produce other active radicals (O₂^{•-} and CO₃^{•-}), is based on the work of Rojas et al. (2010, 2011) and references therein. Since the reactor was open to the atmosphere, the initial carbon dioxide concentration was assumed to be at equilibrium with atmospheric carbon dioxide. The scavenging effect of inorganic carbon species, bicarbonate and carbonate ions was considered in the model, but calculations showed that their effect was negligible in the range of conditions of the experiments.

The rate of direct photolysis of H₂O₂ is given by

$$R_{R1} = -\Phi_{H_2O_2} f_{H_2O_2} I_0 e^{-2.303A_z} \quad (D-1)$$

where $\Phi_{H_2O_2}$ (Table D-1) is the quantum yield for the photocatalytic decomposition of H₂O₂, $f_{H_2O_2}$ is the fraction of total light absorbed by H₂O₂, I_0 is the average fluence rate (in Einsteins per unit time and reactor volume) at the reactor surface and A_z is the total absorbance of the solution as function of depth. In the model, H₂O₂, PC, 4 MC and 4 MB are the only important light-absorbing species at 254 nm. Therefore, A_z is given by

$$A_z = (\epsilon_{H_2O_2}[H_2O_2] + \epsilon_{PC}[PC] + \epsilon_{4MC}[4MC] + \epsilon_{4MB}[4MB])z \quad (D-2)$$

where $\epsilon_{H_2O_2}$, ϵ_{PC} , ϵ_{4MC} (Table D-1) and ϵ_{4MB} (2100 M⁻¹cm⁻¹; Waite 1976; Jongberg et al. 2011) are molar extinction coefficients for hydrogen peroxide, *p*-cresol, 4-

methylcatechol and 4-methylbenzoquinone at 254 nm, respectively, and z is the distance measured downward within the reactive mixture from the top surface. Note that

$$f_{\text{H}_2\text{O}_2} = \frac{\epsilon_{\text{H}_2\text{O}_2} z [\text{H}_2\text{O}_2]}{A_z} \quad (\text{D-3})$$

The volume averaging of equation (D-1) over the batch reactor is, after manipulations,

$$R_{\text{R1}} = -\Phi_{\text{H}_2\text{O}_2} f_{\text{H}_2\text{O}_2} I_0 (1 - e^{-2.303A}) \quad (\text{D-4})$$

where the angular brackets denote volume average, and $A = A_z$ ($z = l$), where l is the depth of the reacting mixture. Other direct photolysis reactions are treated in the same manner.

Radical reactions are generally second-order reactions. For example, the reaction rate for the consumption of *p*-cresol by OH radical is

$$R_{\text{R23}} = -k_{23} [\text{PC}] [\cdot\text{OH}] \quad (\text{D-5})$$

where k_{23} is the second-order rate constant of *p*-cresol reaction with $\cdot\text{OH}$ (Table D-1).

Acid-base reactions are considered to be at equilibrium. The equilibrium equations are used to relate concentrations of the species involved. For example, for acetic acid,

$$[\text{HA}] = \frac{\text{TOT}_A \gamma_{\pm 1} [\text{H}^+]}{K_{36} + \gamma_{\pm 1} [\text{H}^+]} \quad (\text{D-6})$$

$$\gamma_{\pm 1} [\text{A}^-] = \frac{\text{TOT}_A K_{36}}{K_{36} + \gamma_{\pm 1} [\text{H}^+]} \quad (\text{D-7})$$

where $\text{TOT}_A = [\text{HA}] + [\text{A}^-]$, K_{36} is equilibrium constant of acetic acid dissociation and $\gamma_{\pm 1}$ is the activity coefficient, which is calculated from the Davies Equation.

Based on the mechanism proposed, the corresponding mole balances of H_2O_2 , *p*-cresol and 4-methylcatechol yield the following system of differential equations:

$$\begin{aligned} \frac{d[\text{H}_2\text{O}_2]}{dt} = & -\Phi_{\text{H}_2\text{O}_2} f_{\text{H}_2\text{O}_2} I_0 (1 - e^{-2.303A}) - k_2 [\text{H}_2\text{O}_2] [\cdot\text{OH}] + k_8 [\cdot\text{OH}]^2 \\ & - k_{10} [\text{H}_2\text{O}_2] \gamma_{\pm 1} [\text{O}_2^{\cdot-}] + k_{13} [\text{HO}_2^{\cdot}]^2 - k_{14} [\text{H}_2\text{O}_2] [\text{HO}_2^{\cdot}] \\ & - k_{15} [\text{H}_2\text{O}_2] \gamma_{\pm 1} [\text{CO}_3^{\cdot-}] - k_{18} [\text{H}_2\text{O}_2] + k_{18r} \gamma_{\pm 1} [\text{HO}_2^-] \gamma_{\pm 1} [\text{H}^+] \end{aligned} \quad (\text{D-8})$$

$$\frac{d[\text{PC}]}{dt} = -\Phi_{\text{PC}} f_{\text{PC}} I_0 (1 - e^{-2.303A}) - k_{23} [\text{PC}] [\cdot\text{OH}] \quad (\text{D-9})$$

$$\frac{d[4\text{MC}]}{dt} = -\Phi_{4\text{MC}} f_{4\text{MC}} I_0 (1 - e^{-2.303A}) + k_{23} [\text{PC}] [\cdot\text{OH}] - k_{25} [4\text{MC}] [\cdot\text{OH}] \quad (\text{D-10})$$

$$[\text{TOC}] = [\text{TOC}]_0 - [\text{CO}_2] + [\text{CO}_2]_0 \quad (\text{D-11})$$

where $[\text{TOC}]_0$ and $[\text{CO}_2]_0$ are initial TOC and CO_2 molar concentrations. More details of the model formulation, including mole balances of radicals ($\cdot\text{OH}$, $\text{HO}_2^{\cdot}$, $\text{O}_2^{\cdot-}$ and $\text{CO}_3^{\cdot-}$) and reaction intermediates (4 MB, 3 MM, LA^- , OA^- , OA^{2-} , $\text{OA}^{\cdot-}$, AA, AA^- and FA^-), plus algebraic equations ($[\text{H}_2\text{CO}_3]$ as a function of $[\text{TOTCO}_3]$ and charge balance) are provided in the supporting information (APPENDIX D1).

Table D-1. Kinetic and equilibrium parameters used in the model. Acronyms are defined in Figure D-1. Quantum yield (Φ) and molar extinction coefficients (ϵ) are reported for photolysis reactions, kinetic rate constants (k) are reported for relevant reactions, and equilibrium constants (K) are reported for reactions assumed to reach equilibrium instantaneously in the reaction mixture.

Reaction	Parameters	Reference
R1 $\text{H}_2\text{O}_2 + h\nu \rightarrow 2 \cdot\text{OH}$	$\epsilon_1 = 18.7 \text{ M}^{-1}\text{cm}^{-1}$ $\Phi_1 = 0.5 \text{ mol/Ein}$	Volman and Chen (1959)
R2 $\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{O}_2^{\cdot-} + \text{H}_2\text{O} + \text{H}^+$	$k_2 = 2.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R3 $\cdot\text{OH} + \text{HO}_2^{\cdot-} \rightarrow \text{O}_2^{\cdot-} + \text{H}_2\text{O}$	$k_3 = 7.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R4 $\cdot\text{OH} + \text{HCO}_3^{\cdot-} \rightarrow \text{CO}_3^{\cdot-} + \text{H}_2\text{O}$	$k_4 = 8.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R5 $\cdot\text{OH} + \text{CO}_3^{2-} \rightarrow \text{CO}_3^{\cdot-} + \text{OH}^-$	$k_5 = 3.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R6 $\cdot\text{OH} + \text{HO}_2^{\cdot} \rightarrow \text{O}_2 + \text{H}_2\text{O}$	$k_6 = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R7 $\cdot\text{OH} + \text{O}_2^{\cdot-} \rightarrow \text{O}_2 + \text{OH}^-$	$k_7 = 8.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R8 $\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$	$k_8 = 5.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R9 $\cdot\text{OH} + \text{CO}_3^{\cdot-} \rightarrow \text{products}$	$k_9 = 3.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Holcman et al. (1987)
R10 $\text{O}_2^{\cdot-} + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{O}_2 + \text{OH}^-$	$k_{10} = 0.13 \text{ M}^{-1}\text{s}^{-1}$	Bielski et al. (1985)
R11 $\text{O}_2^{\cdot-} + \text{CO}_3^{\cdot-} \rightarrow \text{O}_2 + \text{CO}_3^{2-}$	$k_{11} = 6.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Eriksen et al. (1985)
R12 $\text{O}_2^{\cdot-} + \text{HO}_2^{\cdot} \rightarrow \text{HO}_2^{\cdot-} + \text{O}_2$	$k_{12} = 9.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Benon et al. (1985)
R13 $\text{HO}_2^{\cdot} + \text{HO}_2^{\cdot} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k_{13} = 8.6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	Weinstein and Bielski (1979)
R14 $\text{HO}_2^{\cdot} + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{O}_2 + \text{H}_2\text{O}$	$k_{14} = 3.7 \text{ M}^{-1}\text{s}^{-1}$	Bielski et al. (1985)
R15 $\text{CO}_3^{\cdot-} + \text{H}_2\text{O}_2 \rightarrow \text{HCO}_3^{\cdot-} + \text{O}_2^{\cdot-} + \text{H}^+$	$k_{15} = 8.0 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	Neta et al. (1988)
R16 $\text{CO}_3^{\cdot-} + \text{HO}_2^{\cdot-} \rightarrow \text{HCO}_3^{\cdot-} + \text{O}_2^{\cdot-}$	$k_{16} = 3.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Neta et al. (1988)
R17 $\text{CO}_3^{\cdot-} + \text{CO}_3^{\cdot-} \rightarrow 2\text{CO}_3^{2-}$	$k_{17} = 2.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Neta et al. (1988)
R18 $\text{H}_2\text{O}_2 \leftrightarrow \text{HO}_2^{\cdot-} + \text{H}^+$	$k_{18} = 2.51 \times 10^{-2} \text{ s}^{-1}$ $k_{18r} = 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Perry et al. (1984)
R19 $\text{HO}_2^{\cdot} \leftrightarrow \text{O}_2^{\cdot-} + \text{H}^+$	$k_{19} = 1.58 \times 10^5 \text{ s}^{-1}$ $k_{19r} = 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Perry et al. (1984)
R20 $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$	$k_{20} = 0.039 \text{ s}^{-1}$ $k_{20r} = 23 \text{ s}^{-1}$	Housecroft and Sharpe (2005)
R21 $\text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^{\cdot-} + \text{H}^+$	$k_{21} = 1.25 \times 10^7 \text{ s}^{-1}$ $k_{21r} = 5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Greenwood and Earnshaw (1997)

Table D-1. (Continued)

	Reaction	Parameters	Reference
R22	PC + hv $\rightarrow$ products	$\epsilon_{22} = 340 \text{ M}^{-1}\text{cm}^{-1}$	This work
R23	PC + $\cdot\text{OH} \rightarrow$ 4MC	$\Phi_{22} = 0.034 \text{ mol/Ein}$ $k_{23} = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R24	4MC + hv $\rightarrow$ products	$\epsilon_{24} = 310 \text{ M}^{-1}\text{cm}^{-1}$ $\Phi_{24} = 0.007 \text{ mol/Ein}$	This work
R25	4MC + $\cdot\text{OH} \rightarrow$ 4MB	$k_{25} = 1.6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Gohn and Getoff (1977)
R26	4MB + $\cdot\text{OH} \rightarrow$ 3MM $^{-}$	$k_{26} = 2.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	This work
R27	3MM $^{-}$ + $\cdot\text{OH} \rightarrow$ L $^{-}$ + 2 Ox $^{-}$ (Ox $^{2-}$)	$k_{27} = 5.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Kang et al. (2002)
R28	L $^{-}$ + $\cdot\text{OH} \rightarrow$ HA (A $^{-}$) + CO $_2$ + H $_2$ O	$k_{28} = 3.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R29	Ox $^{-}$ + $\cdot\text{OH} \rightarrow$ Ox $^{\cdot-}$ + H $_2$ O	$k_{29} = 4.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R30	Ox $^{2-}$ + $\cdot\text{OH} \rightarrow$ Ox $^{\cdot-}$ + OH $^{-}$	$k_{30} = 7.7 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R31	Ox $^{\cdot-}$ + Ox $^{\cdot-} \rightarrow$ Ox $^{-}$ (Ox $^{2-}$) + 2 CO $_2$	$k_{31} = 5.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Ershov et al. (2008)
R32	HA + $\cdot\text{OH} \rightarrow$ F $^{-}$ + CO $_2$ + H $_2$ O	$k_{32} = 1.23 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Sun and Saeys (2008)
R33	A $^{-}$ + $\cdot\text{OH} \rightarrow$ F $^{-}$ + CO $_2$ + OH $^{-}$	$k_{33} = 8.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
R34	F $^{-}$ + $\cdot\text{OH} \rightarrow$ CO $_2$ + H $_2$ O	$k_{34} = 9.77 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Sun and Saeys (2008)
E35	Ox $^{-} \leftrightarrow$ Ox $^{2-}$ + H $^{+}$	$K_{35} = 6.31 \times 10^{-5} \text{ M}$	Benjamin (2002)
E36	HA $\leftrightarrow$ A $^{-}$ + H $^{+}$	$K_{36} = 1.74 \times 10^{-5} \text{ M}$	Benjamin (2002)
E37	HCO $_3^{-} \leftrightarrow$ CO $_3^{2-}$ + H $^{+}$	$K_{37} = 4.48 \times 10^{-11} \text{ M}$	Benjamin (2002)

The fact that the reactor is well mixed implies that most species concentrations are uniform in the reactor. However, the relatively high reaction rates of radical species suggest that their concentrations are not necessarily uniform. For example, the OH radical production by reaction R1 (Table D-1) is not uniform due to the attenuation of light with depth. In the model equations, radical concentrations are volume-averaged concentrations. The formulation is based on the assumption that kinetics that are not linear on radical concentrations (such as in radical/radical reactions like R8, Table D-1) can be expressed in terms of volume-averaged radical concentrations. This approximation was explored in detail by Rojas et al. (2010).

The final system of equations was solved using the stiff-differential- equations solver ODE15s in MATLAB (based on Gear's method). The relative tolerance was 10^{-8} , whereas the absolute tolerances for concentrations of all species were set four orders of magnitude below their respective values.

D.3 Results and Discussion

D.3.1 Actinometry. Hydrogen Peroxide Photolysis

The average fluence rate at the surface of the reactor was determined using H_2O_2 actinometry. Hydrogen peroxide direct decomposition experiments were conducted at various initial concentrations. The kinetic model was applied to calculate the reactor surface average fluence rate by fitting experimental data for H_2O_2 decay. Reactions 1—21 (Table D-1) were used in the model formulation. A value of $I_0 = 0.85 \times 10^{-6} \text{ Ein L}^{-1}\text{s}^{-1}$ was obtained (Figure D-2), which was in agreement with the fluence rate measured by the fluence meter.

Figure D-2. Decomposition of hydrogen peroxide in Milli-Q water in the batch reactor. Solid lines: model predictions obtained by fitting the model to decay curves using the fluence rate as adjustable parameter.

D.3.2 *p*-Cresol and 4-Methylcatechol Direct Photolysis

Quantum yields of *p*-cresol and 4-methylcatechol were determined from direct photolysis experiments for each compound separately. In the experiments, *p*-cresol or 4-methylcatechol solutions were exposed to UV light in the absence of H₂O₂. The quantum yield of each compound was calculated by fitting the kinetic model to data representing compound decay. The solution absorbance for all experiments was measured as a function of time to determine A_z (equation (D-2)). This was necessary in direct photolysis experiments since data showed that the products of direct photolysis reaction also absorb 254-nm light. (2,2'-Dihydroxy-5,5'-dimethylbiphenyl, 4-methylcatechol and 2-hydroxy-4',5-dimethyldiphenyl ether have been reported as products in the direct photolysis of *p*-cresol, Joschek and Miller 1966.) Results are presented in Figure D-3. To

generate model predictions, we used the calculated fluence from the actinometry experiments (Figure D-2) and fitted the quantum yields to experimental data.

Figure D-3. Decomposition of (a) *p*-cresol, and (b) 4-methylcatechol in aqueous solution by (LP)UV direct photolysis. Solid lines: model predictions obtained from a fit of model results to decay curves using the respective quantum yield as adjustable parameter. (a) $[PC]_0 = 0.438 \text{ mM}$, (b) $[4 \text{ MC}]_0 = 0.103 \text{ mM}$.

D.3.3 Model Predictions: *p*-Cresol Degradation

Figure D-4 provides predicted and experimental decay curves for *p*-cresol in a series of experiments carried out at different initial concentrations of H₂O₂ and *p*-cresol. Model calculations include the fluence rate determined via actinometry and the quantum yields for *p*-cresol and 4-methylcatechol determined via direct photolysis. In all cases experimental results are accurately predicted by the model. Omitting OH radical scavenging by reaction intermediates significantly overestimates the destruction rate of *p*-cresol in most cases (dashed lines in Figure D-4), which highlights the importance of incorporating the full mechanism in the kinetic model.

Calculations show that intermediates, especially those before ring cleavage (4-methylcatechol and 4-methylbenzoquinone) played an important role in hydroxyl radical quenching. There is no reported kinetic rate constant for the reaction of 4-methylbenzoquinone reaction with hydroxyl radical although Scheck and Frimmel (1995) reported that 1,2-benzoquinone was not detected during oxidation of phenol by the UV/H₂O₂ process because it is easily cleaved into aliphatic compounds. In this study, the rate constant for the reaction of 4-methylbenzoquinone with hydroxyl radical was held to be of the same magnitude as that of 4-methylcatechol, $k_{26} = 2.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, near the diffusion limit. Model results were obtained with no additional fitted parameters; all other rate constants were obtained from preliminary experiments (i.e. actinometry and direct photolysis experiments) or published data (Table D-1).

Figure D-4. Degradation of *p*-cresol in aqueous solution by UV/ H_2O_2 advanced oxidation as a function of initial H_2O_2 concentrations (a), and initial *p*-cresol concentrations (b). Solid lines: full model predictions using the proposed mechanism; dashed lines: model calculations neglecting reactions of intermediates. (a) $[\text{PC}]_0 = 0.1\text{ mM}$, (b) $[\text{H}_2\text{O}_2]_0 = 1\text{ mM}$.

Molecular oxygen participates in several steps of the reaction mechanism—specifically, in the oxidation of 4-methylcatechol to 4-methylbenzoquinone (Davies et al. 1995) and the oxidation of carbon double bonds (Jin et al. 2010; Huang et al. 2011). To test the potential role of oxygen, we performed experiments with degassed solutions by bubbling argon into the solution before exposure to UV light. During the experiment, an argon atmosphere was maintained over the reactor to prevent oxygen diffusion into the reacting mixture. The results in terms of *p*-cresol concentration vs. time showed no appreciable difference relative to the original experiments, suggesting that dissolved oxygen is not important in *p*-cresol oxidation. Representative results are provided in the supporting information (APPENDIX D1).

There are two possible pathways for the OH-induced oxidation of *p*-cresol to 4-methylcatechol (Omura and Matsuura 1968; Scheck and Frimmel 1995): the first involves the cyclohexadienyl radical formed due to OH radical attack that converts the *p*-cresol into dihydroxy compounds. In the second, the phenoxyl radical formed due to the abstraction of hydrogen atom subsequently combines with a second OH radical. However, the second mechanism is dominant only when the OH-radical is present at high concentrations (Waters 1964). In the kinetic model used here, only one OH radical is involved in the conversion of *p*-cresol to 4-methylcatechol, suggesting that the cyclohexadienyl pathway predominates.

The production of 4-methylcatechol was measured in the experiments (Figure D-5). The reaction of *p*-cresol with OH radical was the only 4-methylcatechol source, but two sinks are considered in the kinetic model: direct photolysis and reaction with OH radical. Even though the rate constant for 4-methylcatechol reaction with OH radical is higher than that

Figure D-5. Degradation of *p*-cresol in aqueous solution by UV/H₂O₂ advanced oxidation. Evolution of 4-methylcatechol concentration with time. Solid lines: model predictions. [PC]₀ = 0.5 mM, (a) [H₂O₂]₀ = 1 mM, (b) [H₂O₂]₀ = 5 mM.

of *p*-cresol, 4-methylcatechol accumulates until most of the *p*-cresol is consumed. There was good agreement between data and predictions at low H₂O₂ concentrations (Figure D-

5a), but the model tends to underpredict concentrations of 4-methylcatechol at later times and higher measured concentrations (Figure D-5b) while still trending correctly.

The evolutions of formic acid, acetic acid and oxalic acid concentrations are presented in Figure D-6 for a representative experiment. (Results for *p*-cresol degradation in this experiment are in Figure D-5b.) Although the α -hydrogens next to the carbon double bonds and carboxyl groups are more active under oxidizing conditions, there may be several ways in which to break down the aliphatic acid formed by the ring cleavage. Therefore, the final stages of the mechanism proposed (Figure D-1) may lead to formation of other species. Figure D-7 shows the trajectory of total carbon corresponding to measured concentrations of aliphatic acids along with model calculations for a representative experiment. Both model and data indicate that aliphatic acids accumulate throughout the experiment. By the end of the experiment (180 min), essentially all the *p*-cresol is destroyed (Figure D-5b).

Figure D-6. Evolution of formic acid, acetic acid and oxalic acid concentrations with time. $[PC]_0 = 0.5$ mM, $[H_2O_2]_0 = 5$ mM.

Figure D-7. Evolution of aliphatic reaction intermediates concentration with time. Solid line: model prediction. $[PC]_0 = 0.5$ mM, $[H_2O_2]_0 = 5$ mM.

The concentrations of H_2O_2 and TOC, and pH were measured throughout the experiment and predicted using the kinetic model (Figures D-8 to D-10). Despite some differences, the model adequately predicts trends in H_2O_2 concentration (Figure D-8) and pH (Figure D-9). Previous studies have calculated pH changes during this type of experiment by assuming that the target organics are completely converted into carbon dioxide (Crittenden et al. 1999; Rojas et al. 2010). In our study, a significant drop in pH was observed in the 3-h experiment. However, the drop of pH was due to the formation of organic acids. The lack of CO_2 production (that is, complete mineralization of the target) is evident in the TOC results (Figure D-10) since TOC does not change appreciably during the experiments, as predicted by our model.

Figure D-8. Evolution of H_2O_2 concentration with time. Solid line: model prediction. $[\text{PC}]_0 = 0.5 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 5 \text{ mM}$.

Figure D-9. Evolution of pH with time. Solid line: model prediction. $[\text{PC}]_0 = 0.5 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 5 \text{ mM}$.

Figure D-10. Evolution of TOC with time. Solid line: model prediction. $[\text{PC}]_0 = 0.5 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 5 \text{ mM}$.

D.3.4 Model Predictions: 4-Methylcatechol Degradation

Experiments were carried out with 4-methylcatechol as the initial substrate at different initial hydrogen peroxide concentrations. As anticipated, degradation rate was directly related to the initial hydrogen peroxide concentration within the range of experiments (Figure D-11). Agreement between experimental data and model simulations is observed at 0.2mM H_2O_2 but the model tends to over-estimate degradation rates at higher H_2O_2 concentrations.

Figure D-11. Degradation of 4-methylcatechol in aqueous solution by UV/ H_2O_2 advanced oxidation as a function of initial H_2O_2 concentrations. Solid lines: model predictions. $[4\text{MC}]_0 = 0.1 \text{ mM}$.

D.4 Concluding Remarks

A comprehensive kinetic model was developed to quantify the oxidation of *p*-cresol by UV/ H_2O_2 AOP in a batch reactor. The model was based on known elementary chemical and photo-chemical reactions of the UV/ H_2O_2 photolysis system, together with

experimentally established direct photolysis reactions and proposed OH-radical reactions with intermediates. The kinetics of *p*-cresol decomposition, as well as the main reaction intermediate (4-methylcatechol) was successfully simulated throughout a wide range of operating conditions. The approach employed shows that the full reaction mechanism needs to be considered to evaluate process performance. In particular, reaction intermediates, especially those formed before ring cleavage, play an important role in the quenching of hydroxyl radicals and, consequently, those compounds must be considered in kinetic models of AOP degradation of phenolic compounds.

D.5 References

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APPENDIX D1: Supplementary Materials for APPENDIX D

D1.1 Model of UV/H₂O₂ oxidation of *p*-cresol

In this section, we present the full system of equations that were solved for the kinetic model described in the manuscript. Acronyms are defined in Figure D-1.

$$\begin{aligned} \frac{d[\text{H}_2\text{O}_2]}{dt} = & -\Phi_{\text{H}_2\text{O}_2} f_{\text{H}_2\text{O}_2} I_0 (1 - e^{-2.303A}) - k_2[\cdot\text{OH}][\text{H}_2\text{O}_2] + k_8[\cdot\text{OH}]^2 \\ & -k_{10}\gamma_{\pm 1}[\text{O}_2^{\cdot-}][\text{H}_2\text{O}_2] + k_{13}[\text{HO}_2^{\cdot}]^2 - k_{14}[\text{HO}_2^{\cdot}][\text{H}_2\text{O}_2] \\ & -k_{15}\gamma_{\pm 1}[\text{CO}_3^{\cdot-}][\text{H}_2\text{O}_2] - k_{18}[\text{H}_2\text{O}_2] + k_{18r}\gamma_{\pm 1}[\text{HO}_2^-]\gamma_{\pm 1}[\text{H}^+] \quad \text{Eq (D1-1)} \end{aligned}$$

$$\begin{aligned} \frac{d[\text{HO}_2^-]}{dt} = & -k_3[\cdot\text{OH}]\gamma_{\pm 1}[\text{HO}_2^-] + k_{12}[\text{HO}_2^{\cdot}]\gamma_{\pm 1}[\text{O}_2^{\cdot-}] - k_{16}\gamma_{\pm 1}[\text{CO}_3^{\cdot-}][\text{HO}_2^-] \\ & +k_{18}[\text{H}_2\text{O}_2] - k_{18r}\gamma_{\pm 1}[\text{HO}_2^-]\gamma_{\pm 1}[\text{H}^+] \quad \text{Eq (D1-2)} \end{aligned}$$

$$\begin{aligned} \frac{d[\cdot\text{OH}]}{dt} = & 2\Phi_{\text{H}_2\text{O}_2} f_{\text{H}_2\text{O}_2} I_0 (1 - e^{-2.303A}) - k_2[\cdot\text{OH}][\text{H}_2\text{O}_2] - k_3[\cdot\text{OH}]\gamma_{\pm 1}[\text{HO}_2^-] \\ & -k_4\gamma_{\pm 1}[\text{HCO}_3^-][\cdot\text{OH}] - k_5\gamma_{\pm 2}[\text{CO}_3^{2-}][\cdot\text{OH}] - k_6[\text{HO}_2^{\cdot}][\cdot\text{OH}] \\ & -k_7\gamma_{\pm 1}[\text{O}_2^{\cdot-}][\cdot\text{OH}] - 2k_8[\cdot\text{OH}]^2 - k_9\gamma_{\pm 1}[\text{CO}_3^{\cdot-}][\cdot\text{OH}] \\ & +k_{10}\gamma_{\pm 1}[\text{O}_2^{\cdot-}][\text{H}_2\text{O}_2] + k_{14}[\text{HO}_2^{\cdot}][\text{H}_2\text{O}_2] - k_{23}[\text{PC}][\cdot\text{OH}] \\ & -k_{25}[4\text{MC}][\cdot\text{OH}] - 2k_{26}[4\text{MB}][\cdot\text{OH}] - 4k_{27}\gamma_{\pm 1}[3\text{MM}^-][\cdot\text{OH}] \\ & -k_{28}\gamma_{\pm 1}[\text{L}^-][\cdot\text{OH}] - k_{29}\gamma_{\pm 1}[\text{Ox}^-][\cdot\text{OH}] - k_{30}\gamma_{\pm 2}[\text{Ox}^{2-}][\cdot\text{OH}] \\ & -k_{32}[\text{HA}][\cdot\text{OH}] - k_{33}\gamma_{\pm 1}[\text{A}^-][\cdot\text{OH}] - k_{34}\gamma_{\pm 1}[\text{F}^-][\cdot\text{OH}] \quad \text{Eq (D1-3)} \end{aligned}$$

$$\begin{aligned} \frac{d[\text{HO}_2^\bullet]}{dt} = & -k_6[\text{HO}_2^\bullet][^\bullet\text{OH}] - k_{12}\gamma_{\pm 1}[\text{HO}_2^\bullet][\text{O}_2^{\bullet-}] - 2k_{13}[\text{HO}_2^\bullet]^2 - k_{14}[\text{HO}_2^\bullet][\text{H}_2\text{O}_2] \\ & -k_{19}[\text{HO}_2^\bullet] + k_{19r}\gamma_{\pm 1}[\text{O}_2^{\bullet-}]\gamma_{\pm 1}[\text{H}^+] \end{aligned} \quad \text{Eq (D1-4)}$$

$$\begin{aligned} \frac{d[\text{O}_2^{\bullet-}]}{dt} = & k_2[^\bullet\text{OH}][\text{H}_2\text{O}_2] + k_3[^\bullet\text{OH}]\gamma_{\pm 1}[\text{HO}_2^-] - k_7\gamma_{\pm 1}[\text{O}_2^{\bullet-}][^\bullet\text{OH}] \\ & -k_{10}\gamma_{\pm 1}[\text{O}_2^{\bullet-}][\text{H}_2\text{O}_2] - k_{11}\gamma_{\pm 1}[\text{CO}_3^{\bullet-}]\gamma_{\pm 1}[\text{O}_2^{\bullet-}] - k_{12}\gamma_{\pm 1}[\text{HO}_2^\bullet][\text{O}_2^{\bullet-}] \\ & +k_{15}\gamma_{\pm 1}[\text{CO}_3^{\bullet-}][\text{H}_2\text{O}_2] + k_{16}\gamma_{\pm 1}[\text{CO}_3^{\bullet-}]\gamma_{\pm 1}[\text{HO}_2^-] + k_{19}[\text{HO}_2^\bullet] \\ & -k_{19r}\gamma_{\pm 1}[\text{O}_2^{\bullet-}]\gamma_{\pm 1}[\text{H}^+] \end{aligned} \quad \text{Eq (D1-5)}$$

$$\begin{aligned} \frac{d[\text{TotCO}_3]}{dt} = & -k_4\gamma_{\pm 1}[\text{HCO}_3^-][^\bullet\text{OH}] - k_5\gamma_{\pm 2}[\text{CO}_3^{2-}][^\bullet\text{OH}] + k_{11}\gamma_{\pm 1}[\text{CO}_3^{\bullet-}]\gamma_{\pm 1}[\text{O}_2^{\bullet-}] \\ & +k_{15}\gamma_{\pm 1}[\text{CO}_3^{\bullet-}][\text{H}_2\text{O}_2] + k_{16}\gamma_{\pm 1}[\text{CO}_3^{\bullet-}]\gamma_{\pm 1}[\text{HO}_2^-] + k_{28}\gamma_{\pm 1}[\text{L}^-][^\bullet\text{OH}] \\ & +2k_{31}\gamma_{\pm 1}[\text{Ox}^{\bullet-}]\gamma_{\pm 1}[\text{Ox}^{\bullet-}] + k_{32}[\text{HA}][^\bullet\text{OH}] + k_{33}\gamma_{\pm 1}[\text{A}^-][^\bullet\text{OH}] \\ & +k_{34}\gamma_{\pm 1}[\text{F}^-][^\bullet\text{OH}] \end{aligned} \quad \text{Eq (D1-6)}$$

$$\begin{aligned} \frac{d[\text{CO}_2(\text{aq})]}{dt} = & k_{28}\gamma_{\pm 1}[\text{L}^-][^\bullet\text{OH}] + 2k_{31}\gamma_{\pm 1}[\text{Ox}^{\bullet-}]\gamma_{\pm 1}[\text{Ox}^{\bullet-}] + k_{32}[\text{HA}][^\bullet\text{OH}] \\ & +k_{33}\gamma_{\pm 1}[\text{A}^-][^\bullet\text{OH}] + k_{34}\gamma_{\pm 1}[\text{F}^-][^\bullet\text{OH}] - k_{20}[\text{CO}_2(\text{aq})] \\ & +k_{20r}[\text{H}_2\text{CO}_3] \end{aligned} \quad \text{Eq (D1-7)}$$

$$\frac{d[\text{H}_2\text{CO}_3]}{dt} = k_{20}[\text{CO}_2(\text{aq})] - k_{20r}[\text{H}_2\text{CO}_3] - k_{21}[\text{H}_2\text{CO}_3] + k_{21r}[\text{HCO}_3^-][\text{H}^+] \quad \text{Eq (D1-8)}$$

$$\begin{aligned}
\frac{d[\text{CO}_3^{\bullet-}]}{dt} = & k_4\gamma_{\pm 1}[\text{HCO}_3^-][\cdot\text{OH}] + k_5\gamma_{\pm 2}[\text{CO}_3^{2-}][\cdot\text{OH}] - k_9\gamma_{\pm 1}[\text{CO}_3^{\bullet-}][\cdot\text{OH}] \\
& -k_{11}\gamma_{\pm 1}[\text{CO}_3^{\bullet-}]\gamma_{\pm 1}[\text{O}_2^{\bullet-}] - k_{15}\gamma_{\pm 1}[\text{CO}_3^{\bullet-}][\text{H}_2\text{O}_2] - k_{16}\gamma_{\pm 1}[\text{CO}_3^{\bullet-}]\gamma_{\pm 1}[\text{HO}_2^-] \\
& -2k_{17r}\gamma_{\pm 1}[\text{CO}_3^{\bullet-}]\gamma_{\pm 1}[\text{CO}_3^{\bullet-}]
\end{aligned} \tag{D1-9}$$

$$\frac{d[\text{PC}]}{dt} = -\Phi_{\text{PC}}f_{\text{PC}}I_o(1 - e^{-2.303A}) - k_{23}[\text{PC}][\cdot\text{OH}] \tag{D1-10}$$

$$\begin{aligned}
\frac{d[4\text{MC}]}{dt} = & -\Phi_{4\text{MC}}f_{4\text{MC}}I_o(1 - e^{-2.303A}) + k_{23}[\text{PC}][\cdot\text{OH}] - k_{25}[4\text{MC}][\cdot\text{OH}] \\
& \tag{D1-11}
\end{aligned}$$

$$\frac{d[4\text{MB}]}{dt} = k_{25}[4\text{MC}][\cdot\text{OH}] - k_{26}[4\text{MB}][\cdot\text{OH}] \tag{D1-12}$$

$$\frac{d[3\text{MM}^-]}{dt} = k_{26}[4\text{MB}][\cdot\text{OH}] - k_{27}\gamma_{\pm 1}[3\text{MM}^-][\cdot\text{OH}] \tag{D1-13}$$

$$\frac{d[\text{L}^-]}{dt} = k_{27}\gamma_{\pm 1}[3\text{MM}^-][\cdot\text{OH}] - k_{28}\gamma_{\pm 1}[\text{L}^-][\cdot\text{OH}] \tag{D1-14}$$

$$\begin{aligned}
\frac{d[\text{TotOx}]}{dt} = & 2k_{27}\gamma_{\pm 1}[3\text{MM}^-][\cdot\text{OH}] - k_{29}\gamma_{\pm 1}[\text{Ox}^-][\cdot\text{OH}] - k_{30}\gamma_{\pm 2}[\text{Ox}^{2-}][\cdot\text{OH}] \\
& + k_{31}\gamma_{\pm 1}[\text{Ox}^{\bullet-}]\gamma_{\pm 1}[\text{Ox}^{\bullet-}]
\end{aligned} \tag{D1-15}$$

$$\begin{aligned}
\frac{d[\text{Ox}^{\bullet-}]}{dt} = & k_{29}\gamma_{\pm 1}[\text{Ox}^-][\cdot\text{OH}] + k_{30}\gamma_{\pm 2}[\text{Ox}^{2-}][\cdot\text{OH}] \\
& -k_{31}\gamma_{\pm 1}[\text{Ox}^{\bullet-}]\gamma_{\pm 1}[\text{Ox}^{\bullet-}]
\end{aligned} \tag{D1-16}$$

$$\frac{d[\text{TotA}]}{dt} = k_{28}\gamma_{\pm 1}[\text{L}^-][\cdot\text{OH}] - k_{32}[\text{HA}][\cdot\text{OH}] - k_{33}\gamma_{\pm 1}[\text{A}^-][\cdot\text{OH}] \tag{D1-17}$$

$$\frac{d[F^-]}{dt} = k_{32}[HA][\bullet OH] + k_{33}\gamma_{\pm 1}[A^-][\bullet OH] - k_{34}\gamma_{\pm 1}[F^-][\bullet OH] \quad \text{Eq (D1-18)}$$

$$[H^+] = [OH^-] + [HO_2^-] + [O_2^{\bullet -}] + [CO_3^{\bullet -}] + [HCO_3^-] + 2[CO_3^{2-}] + [3MM^-] \\ + [L^-] + [Ox^-] + [Ox^{\bullet -}] + 2[Ox^{2-}] + [A^-] + [F^-] \quad \text{Eq (D1-19)}$$

$$\gamma_{\pm 1}[HCO_3^-] = \frac{[TotCO_3]}{\left\{ \frac{\gamma_{\pm 1}[H^+]}{k_{20}k_{21}/k_{20r}k_{21r}} + \frac{\gamma_{\pm 1}[H^+]}{k_{21}/k_{21r}} + 1 + \frac{K_{37}}{\gamma_{\pm 1}[H^+]} \right\}} \quad \text{Eq (D1-20)}$$

$$\gamma_{\pm 2}[CO_3^{2-}] = \frac{K_{37}\gamma_{\pm 1}[HCO_3^-]}{\gamma_{\pm 1}[H^+]} \quad \text{Eq (D1-21)}$$

$$\gamma_{\pm 1}[Ox^-] = \frac{[TotOx]}{\left\{ 1 + \frac{K_{35}}{\gamma_{\pm 1}[H^+]} \right\}} \quad \text{Eq (D1-22)}$$

$$\gamma_{\pm 2}[Ox^{2-}] = \frac{K_{35}\gamma_{\pm 1}[Ox^-]}{\gamma_{\pm 1}[H^+]} \quad \text{Eq (D1-23)}$$

$$[HA] = \frac{[TotA]}{\left\{ 1 + \frac{K_{36}}{\gamma_{\pm 1}[H^+]} \right\}} \quad \text{Eq (D1-24)}$$

$$\gamma_{\pm 1}[A^-] = \frac{K_{36}[HA]}{\gamma_{\pm 1}[H^+]} \quad \text{Eq (D1-25)}$$

where activity coefficients γ are calculated from the Davies Equation

$$\log(\gamma_{\pm 1}) = -0.51 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad \text{Eq (D1-26)}$$

$$\log(\gamma_{\pm 2}) = -2.04 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad \text{Eq (D1-27)}$$

and I is ionic strength of the solution, which is calculated from the concentration of all ionic species in terms of the charge number for each species, z_i , by

$$I = \frac{1}{2} \sum [C_i] z_i^2 \quad \text{Eq (D1-28)}$$

Model calculations yield concentration of all species as a function of time. For radicals, the concentration found is a volume-averaged concentration.

D1.2

Figure D1-1. Degradation of *p*-cresol in aqueous solution by UV/H₂O₂ advanced oxidation in the presence/absence of oxygen. [PC]₀ = 0.5 mM, (b) [H₂O₂]₀ = 1 mM.