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Development of surrogate correlation models to predict trace organic contaminant oxidation and microbial inactivation during ozonation

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ABSTRACT

The performance of ozonation in wastewater depends on water quality and the ability to form hydroxyl radicals (•OH) to meet disinfection or contaminant transformation objectives. Since there are no on-line methods to assess ozone and •OH exposure in wastewater, many agencies are now embracing indicator frameworks and surrogate monitoring for regulatory compliance. Two of the most promising surrogate parameters for ozone-based treatment of secondary and tertiary wastewater effluents are differential UV_{254} absorbance

Abbreviations: AFU, arbitrary fluorescence unit; AOP, advanced oxidation process; AWWTP, Australian (anonymous) Wastewater Treatment Plant; BAC, biological activated carbon; BDF, buffered demand free; CCWRD, Clark County Water Reclamation District; CDPH, California Department of Public Health; CFU, colony forming unit; CLV, City of Las Vegas; CT, concentration × time (as in disinfection); DEET, *N,N*-diethyl-meta-toluamide; EDC, endocrine disrupting compound; EEM, excitation–emission matrix; EfOM, effluent organic matter; FAT, full advanced treatment; GCGA, Gwinnett County Georgia; GC–MS, gas chromatography mass spectrometry; IPR, indirect potable reuse; KOWWTP, Kloten–Opfikon Wastewater Treatment Plant; LC–MS, liquid chromatography mass spectrometry; LWWTP, Lausanne Wastewater Treatment Plant; MBR, membrane bioreactor; MPN, most probable number; MRL, method reporting limit; MWRDGC, Metropolitan Water Reclamation District of Greater Chicago; pCBA, para-chlorobenzoic acid; IPR, indirect potable reuse; PCU, Pinellas County Utilities; PEG, polyethylene glycol; PFU, plaque forming unit; PPCPs, pharmaceuticals and personal care products; RWWTP, Regensdorf (Wüeri) Wastewater Treatment Plant; TCEP, tris-(2-chloroethyl)-phosphate; TF, total fluorescence; TOC, total organic carbon; TOrCs, trace organic contaminants; TSA, tryptic soy agar; TSB, tryptic soy broth; U.S., United States; UV, ultraviolet; WBMWD, West Basin Municipal Water District.

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(ΔUV_{254}) and total fluorescence (ΔTF). In the current study, empirical correlations for ΔUV_{254} and ΔTF were developed for the oxidation of 18 trace organic contaminants (TOrCs), including 1,4-dioxane, atenolol, atrazine, bisphenol A, carbamazepine, diclofenac, gemfibrozil, ibuprofen, meprobamate, naproxen, N,N-diethyl-meta-toluamide (DEET), para-chlorobenzoic acid (pCBA), phenytoin, primidone, sulfamethoxazole, triclosan, trimethoprim, and tris-(2-chloroethyl)-phosphate (TCEP) ($R^2 = 0.50$–0.83) and the inactivation of three microbial surrogates, including *Escherichia coli*, MS2, and *Bacillus subtilis* spores ($R^2 = 0.46$–0.78). Nine wastewaters were tested in laboratory systems, and eight wastewaters were evaluated at pilot- and full-scale. A predictive model for •OH exposure based on ΔUV_{254} or ΔTF was also proposed.

1. Introduction

Trace organic contaminants (TOrCs) pose a challenge for wastewater treatment facilities due to an increased awareness of their ubiquity, the ambiguity of public and aquatic health implications, the high costs associated with their quantification, and the paucity of regulatory guidance. The use of ozone for the transformation of TOrCs, including pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs), has been studied extensively in the literature (Huber et al., 2003, 2004; Buffle et al., 2006; Lee et al., 2008; Dodd et al., 2009; von Sonntag and von Gunten, 2012). Studies specifically addressing the efficacy of ozone for TOrC elimination, reductions in estrogenicity, and the effects on toxicity have also been performed in pilot- and full-scale systems (Huber et al., 2005; Hollender et al., 2009; Wert et al., 2009a; Stalter et al., 2010a, 2010b; Gerrity et al., 2011a; Gerrity and Snyder, 2011; Zimmermann et al., 2011). Ozone is also effective for the inactivation of a wide range of microbial indicators and pathogens (Driedger et al., 2001; Burns et al., 2007; Gerrity et al., 2011a).

This demonstrated efficacy for TOrC mitigation and disinfection has established ozone as a viable option for wastewater treatment. Ozone-based treatment trains are also becoming increasingly popular in indirect potable reuse (IPR) applications as an alternative to membrane filtration, reverse osmosis, and UV/H_2O_2, which is described as full advanced treatment (FAT) by the California Department of Public Health (CDPH) in the United States (U.S.) (CDPH, 2011). By combining ozone with downstream biological filtration, this alternative treatment train is capable of providing a finished water quality similar to that of FAT, albeit at potentially reduced costs (Hollender et al., 2009; Reungoat et al., 2010; Stalter et al., 2010a, 2010b; Gerrity et al., 2011a; Reungoat et al., 2012; Zimmermann et al., 2011).

In wastewater applications, particularly when supplemented with hydrogen peroxide, ozonation can be considered an advanced oxidation process (AOP) due to its rapid decomposition into hydroxyl radicals (•OH). In contrast with drinking water applications (Kaiser et al., submitted for publication), there are no on-line methods to measure ozone and •OH exposure in wastewater so the "CT" approach typically associated with chlorine disinfection (i.e., the product of oxidant concentration and time) cannot be applied to estimate treatment performance. Also, frequent monitoring for TOrCs and pathogens is a costly and time-consuming proposition. As a result, many agencies are embracing indicator frameworks and highlighting the need for surrogate monitoring (Dickenson et al., 2009). For example, CDPH recently published a revised set of draft regulations for groundwater replenishment, which outlines required removals for indicator compounds based on their chemical structures and functional groups (e.g., hydroxyl aromatic, saturated aliphatic). Although these specified removals apply only to advanced oxidation in FAT applications (i.e., reverse osmosis permeate), the framework can be applied more broadly as a TOrC mitigation baseline. In addition to the specified removals, CDPH also requires FAT facilities to identify at least one surrogate parameter that can be monitored continuously, predict the level of oxidation for the indicator compounds, and alert operators to process inefficiencies and failures. Several common water quality parameters associated with bulk organic matter, specifically differential UV absorbance (ΔUV) and total fluorescence (ΔTF), offer particularly promising solutions for this type of application.

Currently, there are few studies that describe the relationships between changes in bulk organic matter, contaminant destruction, and microbial inactivation. Studies using fluorescence as part of an analytical method to detect TOrCs are becoming more common (Camacho-Munoz et al., 2009), but the goal of these studies is inherently different than using changes in bulk organic matter to estimate oxidation efficacy. Although the high sensitivity of fluorometers offers a promising tool for detection of individual contaminants, this method is hindered by interferences from background effluent organic matter (EfOM) in wastewater applications (Fig. S1). Therefore, ΔUV—more specifically, ΔUV_{254}—and ΔTF currently offer the most promising tools to supplement existing analytical methods based on liquid or gas chromatography and mass spectrometry (LC–MS or GC–MS).

Buffle et al. (2006) proposed the use of ΔUV to determine ozone exposure in wastewater applications after observing a first-order kinetic relationship between the two parameters. Based on this concept, Bahr et al. (2007), Wert et al. (2009b), and Nanaboina and Korshin (2010) developed preliminary correlations between ΔUV_{254} and several indicator compounds and microbes. Bahr et al. (2007) presented the linear regression parameters in relation to second-order ozone and •OH rate constants. Wert et al. (2009b) indicated that ozone-susceptible target compounds (i.e., $k_{O_3} > 10^3\ M^{-1}\ s^{-1}$) demonstrated strong