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Strategies for selecting indicator compounds to assess attenuation of emerging contaminants during UV advanced oxidation processes

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Abstract

A ranking system for monitoring-based process control was developed to select indicator compounds that can predict the attenuation of a broader range of trace organic compounds (TOrcs) in reclaimed water by low pressure (LP) and medium pressure (MP)-UV advanced oxidation processes (AOPs). The selected TOrcs were classified into three groups depending on their relative reactivity to UV direct photolysis and $\bullet\text{OH}$ oxidation. Group 1 includes the photolabile TOrcs, which are easily photodegraded with no additional oxidants by either LP or MP-UV light and include acesulfame, diclofenac, and sulfamethoxazole. Group 2 consists of the moderate photodegradable compounds with high reactivity of $\bullet\text{OH}$ oxidation, which include benzotriazole, fluoxetine, and hydrochlorothiazide as indicator compounds for assessing LP-UV AOP and propranolol, diltiazem, and diphenhydramine for MP-UV AOP. Group 3 is photo-resistant TOrcs, but highly reactive with $\bullet\text{OH}$ radicals and includes carbamazepine and DEET as appropriate indicator compounds. Therefore, the proposed ranking system is expected to provide a comprehensive monitoring tool to water reuse utilities for prioritizing a list of indicators to assess the treatment efficacy of UV AOPs that allows for subsequent operational control to achieve the treatment goal. This is the first strategic framework and guidelines for building a customizable tool of process control that depend on the site-specific occurrence profile of wastewater effluents and the UV system (UV lamp spectral output and power density).

Keywords

Water reuse; Ultraviolet advanced oxidation process (UV AOP); Trace organic compounds (TOrcs); Indicator; Photolysis; Hydroxyl radical oxidation

1. Introduction

With burgeoning population and climate change, water shortage throughout the world has highlighted the challenges to augment drinking water supplies through water reclamation using municipal wastewater for potable reuse. Municipal wastewater contains a wide range of chemical and biological contaminants, some of which could be potentially harmful to public health and ecosystems (National Research Council, 2012). One of the challenges associated with potable water reuse is the removal of trace organic compounds (TOCs) or contaminants of emerging concern (CECs) including pharmaceuticals and personal care products (PPCPs), endocrine disrupting compounds (EDCs), and industrial chemicals in wastewater.

To minimize adverse impacts on public health by wastewater-derived chemical contaminants, advanced oxidation processes (AOPs) have been employed to attenuate such chemical compounds that are not completely removed through conventional wastewater treatment processes (Snyder, 2008, Stefan, 2018). Ultraviolet (UV)-mediated AOPs have increasingly gained attention due to the effectiveness for the attenuation of wide range of TOCs as well as disinfection using two types of UV lamps. Low pressure (LP) UV lamps emit monochromatic light at 254 nm and medium pressure (MP) UV lamps release polychromatic, broad-band spectrum from 200 to 400 nm. Kinetic models are necessary for prediction of system performance and treatment efficiency under both UV direct photolysis and AOP involving hydroxyl radical ($\bullet\text{OH}$). However, application of these models is limited due in part to the difficulties of finding the photolysis parameters such as molar absorption coefficient and quantum yield for each constituent, which are wavelength-dependent. This is especially true when a polychromatic light source is used (Hokanson et al., 2016), conversely the $\bullet\text{OH}$ oxidation rate constants of many TOCs have been previously reported in many studies and vary from 10^7 and $10^{10} \text{ M}^{-1}\text{s}^{-1}$ (Sanches et al., 2010, Wu and Linden, 2010).

One of the main challenges for the application of UV AOP for potable water reuse is the need for monitoring and related process control to ensure attenuation efficacy of organic compounds through the treatment process (Yu et al., 2015). Due to the large number of wastewater-derived TOrCs, frequent monitoring of each compound is vastly infeasible in terms of associated labor, time, and analytical costs. Consequently, water utilities and regulatory authorities are highlighting the need for simplified indicator frameworks to assess the efficiency of AOP treatment and to facilitate regulatory compliance (Dickenson et al., 2009, Gerrity et al., 2012). Indicator compounds are individual chemicals capable of mimicking the behavior of broader classes of compounds, which requires (1) frequent occurrence at concentrations significantly above the analytical detection limit; and (2) representative behavior of a particular family or group of compounds over the course of a treatment process. In addition, reclamation facilities often desire monitoring and operational systems to predict the attenuation level of TOrCs to alert operators to process inefficiencies and treatment system malfunctions in order to ensure that reclaimed water meets the appropriate quality standards (such as Title 22 of California's Water Recycling Criteria by California Department of Public Health (CDPH)). Recently, the indicator and surrogate monitoring framework have been investigated for LP-UV AOP (Yu et al., 2015) and ozonation (Gerrity et al., 2012), but only sparse data exist regarding selection of appropriate indicator chemicals to evaluate process efficiency during UV AOP, especially using for medium pressure (MP) polychromatic UV processes. This is due in part to the lack of adequate data on photochemical parameters of a broad range of TOrCs.

Therefore, the objective of this study is to propose a ranking system to select viable indicator compounds that represent different photochemical groups depending on their relative reactivity to UV direct photolysis and $\bullet\text{OH}$ oxidation, and to evaluate attenuation efficiency of TOrCs during LP- and MP-UV AOP treatment of reclaimed water. The framework for selecting indicator compounds was investigated in three ways: (1) determination of photokinetic parameters such as molar absorption coefficient and quantum yield under UV irradiation at monochromatic and

polychromatic wavelengths, (2) categorization of TOrCs based on UV dose or electric energy required depending their efficiency of photolytic degradation, and (3) development of ranking system to select the appropriate indicator compound to assess the process performance based on occurrence level of TOrCs in wastewater effluents and photochemical reactivity in response to UV direct photolysis and $\bullet\text{OH}$ oxidation during UV AOPs. The following framework and guidelines are meant to bring clarity to customizing the ranking system tool and help operators choose the suitable indicator compound to predict process performance for their own purposes. The intent is to provide the insight regarding customizing practices that depend on the site-specific occurrence profile of wastewater effluents and the UV system (UV lamp spectral output and power density).

2. Material and Methods

2.1. Determination of photokinetic parameters: molar absorption coefficient and quantum yield

For measuring molar absorption coefficients, three serial dilutions of each TOrC (2.5, 5, 10 mg L⁻¹) were prepared separately in Milli-Q water, and were then measured by a UV/Vis spectrophotometer (Cary 50, Agilent) at a path length of 1 cm over the wavelengths 200 – 320 nm. The absorbance of each dilution was measured in triplicates and the molar absorption coefficient was calculated for each dilution by dividing the measured absorbance with the analyzed concentration. Finally, the measured values were averaged at each wavelength to obtain the molar absorption coefficient in the 200-320 nm region for each TOrCs.

To determine UV dose-based first-order rate constants and quantum yields of individual contaminants, 30 mL of each TOrCs solution (100 $\mu\text{g L}^{-1}$) in Petri dish was exposed to UV doses of 0, 400, 800, 1200 mJ cm^{-2} with mild constant stirring, and was then taken for immediate analysis.

2.2. Direct UV photolysis using a collimated beam device

A collimated beam UV apparatus (CBD 11-1, ITT Water & Wastewater Herford GmbH, Wedeco) equipped with 4 LP-UV Hg lamps (NLR2036) or MP-UV Hg lamps (ZKM10) were used to expose each TOrCs solution with monochromatic light at 254 nm or polychromatic light between 200 to 320 nm, respectively. The UV irradiances (fluence rates) of LP and MP-UV lamps were measured by the calibrated UV detectors (SED240/NS254/W for LP-UV and SED240/W for MP-UV, International Light) connected to a radiometer (IL 1700, International Light), which was multiplied by correction factors based on (Bolton and Linden, 2003):

$$E = E_0 \times PF \times RF \times DF \times WF \quad (\text{Eq.1})$$

where E is the average UV fluence rate (mW cm^{-2}); E_0 is the radiometer reading at the surface of liquid in the Petri dish and at the center of the UV beam (mW cm^{-2}); PF is the Petri factor (non-uniformity of radiation field across the dish); RF is the reflection factor (fraction of the incident beam that enters the water); DF is the divergence factor (attenuation of the UV beam due to the distance between light source and solution); and WF is the water factor (attenuation of the UV beam within the liquid due to the solution absorption). For polychromatic light, WF of TOrCs samples must be integrated and corrected over the wavelength of 200 – 320 nm.

Though at different UV fluence rates of mono and polychromatic light sources, the UV photons entering the actinometer solution were kept the same (as represented by UV fluence or dose (mJ cm^{-2}), which equals to UV fluence rate (mW cm^{-2}) multiplied by the exposure time (s)). The following results interpretation and discussion will mainly thus focus on the use of UV dose instead of irradiation time except stated otherwise.

2.3. Analysis of TOrCs using triple quadrupole LC-MS/MS

Thirty six TOrCs were analyzed as classes of pharmaceuticals, personal care products, industrial compounds, pesticides, and hormones, according to the previously developed analytical methods (SI 1 and Table S1) (Anumol and Snyder, 2015, Anumol et al., 2013).

2.4. Determination of electrical energy per order (EEO)

Since the pollutant is normally in relatively low concentrations (< 100 mg/L) in most AOP applications in water treatment, it is useful to calculate the electrical energy used per order of magnitude reduction which can be calculated from Electrical Energy Dose (EED) for a given process (Bolton et al., 2001, Malley, 2008):

$$\text{EED (kWh/m}^3\text{)} = (P \cdot T) / 60 V \quad (\text{Eq. 3})$$

$$\text{EEO (kWh/m}^3\text{.order)} = \text{EED} / (\log C_0/C) \quad (\text{Eq. 4})$$

where, P is the electric power (kW), T is the irradiation time (min), V is the total system volume (m^3), C_0 and C is the concentration of TOrCs before and after UV exposure, respectively.

It is useful to linearize this equation to determine EEO for a given set of data:

$$\log C = \log C_0 + (-1/\text{EEO})(\text{EED}) \quad (\text{Eq. 5})$$

Experimental data can then be plotted as C versus EED and the resulting slope is equivalent to $-1/\text{EEO}$ which allows computation of the EEO based on the fact that the selected compounds all follow pseudo first-order decay kinetics.

3. Results and Discussion

3.1. Photochemical parameters of direct UV photolysis: molar absorption coefficient and quantum yield

When an oxidant is added to the water during UV AOPs, the hydroxyl radical ($\bullet\text{OH}$), an unselective, short-lived, and powerful oxidant ($E_0 = 2.3 \text{ V}$, pH 7), is produced under UV irradiation. This radical quickly reacts with TOrCs through hydrogen atom extraction and electron transfer, with second-order rate constants above $10^9 \text{ M}^{-1}\text{s}^{-1}$ (Table S3 and S4), while the photolytic degradation kinetic

is mainly governed by direct UV photolysis. The photochemical process induced by the radiation in a chemical compound is determined by two critical parameters: the probability of the light absorption event, which depends on the optical properties of the compound that are quantified in its absorption spectrum, and the probability that the excited state reached through the light absorption process proceeds to a chemical reaction, which is expressed as the quantum yield. It should be recognized that photolysis sometimes triggers a chain of reactions involving free radicals of other kinds, which can cause the rate of chemical transformation as a result of photolysis to be influenced by the chemistry of the surrounding water (Hokanson et al., 2016). The discussion is confined to the direct photolysis mechanism itself where constituents are transformed by UV light alone.

3.1.1. Molar absorption coefficient

Photolysis, photo-dissociation, or photo-decomposition is a chemical reaction in which a chemical compound is broken down by photons with sufficient energy required for chemical bond dissociation. Since a photon's energy is inversely proportional to its wavelength (λ), electromagnetic waves with the relatively higher energy of ultraviolet light (UV) are usually involved in such reactions. Theoretically, any radiation of $\lambda < \lambda_D$ (threshold wavelength (nm), defined as the maximum wavelength for which the photon energy matches the bond energy required to result in a homolytic bond cleavage), carrying energies $E_\lambda > E_{\lambda D}$ can break the corresponding chemical bond, as a result of light absorption. The absorption spectrum characteristics depend on the molecular structure of a specific compound. Most absorbers of UV light (UV-C 200–280 nm, UV-B 280–320 nm, UV-A 320–400 nm) contain double bonds or conjugated double bonds, involving carbon, oxygen or nitrogen atoms, and are characterized by delocalized π -electrons, which are called chromophores. The environmental contaminants containing chromophoric structures include alkenes, aromatic and heterocyclic compounds, aldehydes, ketones, and carboxylic acids, and nitro- and nitroso-derivatives. However, the

saturated compounds containing the same atoms do not absorb the light with 205–210 nm (Parsons, 2004). Therefore, the capacity of a compound absorbing photons of the incident light is an important factor for its photochemical reaction.

The decadic molar absorption coefficient (ϵ) measures the probability that a compound can absorb light at a particular wavelength (λ), obtained by dividing the measured absorbance (A) of solutions spiked with each TOrCs at a given wavelength by the molar concentration (M) using a 1 cm path length (z) according to Beer–Lambert law, $\epsilon(\lambda) = A(\lambda)/[\text{TOrCs}] \cdot z$. The resulting molar absorption coefficient (ϵ) of each TOrCs over the UV light wavelength range are presented with the normalized emission spectrum of the LP and MP-UV lamps in Fig. 1 and Fig. S1. It is important to match output spectra of UV lamp with target compound absorption spectra, because photochemical reactions cannot occur unless photons of the emitted UV light are adsorbed by the target compound based on the first law of photochemistry (Wayne et al., 1996). These spectra show that the strong absorption bands observed for each TOrCs mostly within UV-C and UV-B regions between 200 and 320 nm, which means that the irradiations by both LP and MP-UV lamps are efficient in photodegrading the selected TOrCs by direct photolysis.

The measured capacity of each TOrCs to absorb the photons emitted by LP-UV (ϵ_{254}) and MP-UV ($\epsilon_{200-320}$) lamp sources is shown in Table 1. For polychromatic light released from MP-UV lamp, the integrated molar absorption coefficient ($\epsilon_{200-320}$) was calculated as the sum of the absorption coefficients over the entire band, and corresponds to the area under the plot of the molar absorption coefficient against the wavelength of the incident radiation (Atkins and Paula, 2010). Compared to LP-UV lamp, the photolysis by polychromatic radiation might be more effective since the MP-UV lamp covers wider range of wavelengths in the UV-C and UV-B region than the monochromatic light at 254 nm, and more photons can be absorbed at lower wavelengths. This increases the probability that the photons of different wavelengths undergo excitation and chemical reactions leading to bond breakage and rearrangement (Wols et al., 2013, Wols et al., 2015). Organic compounds with higher molar absorptivity thus have a higher potential for direct

photolytic degradation. It was also observed that each compound has the specific maximum absorption bands at different wavelengths that strongly excites molecules to high electronic states, which can subsequently lead to bond cleavage (Fig. 1 and Fig. S1). Besides the molar absorption coefficient, quantum yield (Φ) is another fundamental parameter governing the rate of direct photolytic degradation to measure a compound's amenability to transformation when exposed to light and to evaluate the efficiency of a photochemical process.

Fig. 1. Overlaid molar absorption coefficient of all TORCs and spectral output of LP and MP-UV lamps evaluated in this study

3.1.2. Quantum yield

The quantum yield (Φ) is a fundamental unitless parameter that quantifies the photon efficiency of a photochemical reaction, representing the ratio of the total number of molecules of the compound transformed (mol) to total number of photons absorbed by a compound due to the compound's presence (E) (Schwarzenbach et al., 2002). It can be determined from the UV dose-based first-order rate constant (Stefan and Bolton, 2005):

$$\Phi = \frac{10k'_d}{\ln(10) \sum_{\lambda} \frac{N(\lambda)\varepsilon(\lambda)}{U(\lambda)}} \quad (\text{Eq. 2})$$

where k'_d is the UV dose-based rate constant ($\text{m}^2 \text{J}^{-1}$), $N(\lambda)$ are the relative photon flows emitted by the light source for narrow wavelength bands from 200 – 320 nm, and $U(\lambda)$ (J E^{-1}) is the energy of one mole of photons at wavelength λ . $\varepsilon(\lambda)$ is the molar absorption coefficient ($\text{M}^{-1} \text{cm}^{-1}$) at wavelength λ . Pseudo first-order degradation was observed for all the selected compounds for direct UV photolysis. The quantum yields (Φ), and UV dose-based pseudo first-order rate constants of direct photolysis (k'_d) for all the model compounds in this study are given in Table 1. Compounds with larger k'_d values are more desirable, as they are more susceptible to UV photolysis, and consequently less electrical energy is required to achieve the treatment goal. It can thus be a useful tool in assessing the treatment efficacy for a UV system (Hokanson et al., 2016).

The TOrCs degradation kinetics by direct photolysis can be modeled using the following expression (Schwarzenbach et al., 2002, Sharpless and Linden, 2003):

$$-\frac{d[\text{TOrCs}]}{dt} = k_d[\text{TOrCs}] = \left(\sum_{\lambda} K_s(\lambda) \right) \phi(\lambda)[\text{TOrCs}] \quad (\text{Eq. 6})$$

$$K_s(\lambda) = \frac{E_p^0(\lambda)\varepsilon(\lambda)[1 - 10^{-a(\lambda)z}]}{a(\lambda)z} \quad (\text{Eq. 7})$$

where, k_d represents the time-based pseudo-first-order rate constant of each compound (s^{-1}); it can be obtained from the linear slope of a plot of $\ln([C_0]/[C])$ versus exposure time for the direct

photolysis. If $\ln([C_0]/[C])$ is plotted versus the UV dose (mJ cm^{-2}), one can obtain the corresponding direct photolysis fluence-based rate constant, k'_d (Bolton and Stefan, 2002). $K_s(\lambda)$ is the specific rate of light absorption by the compound ($\text{E mol}^{-1}\text{s}^{-1}$), $E_p^0(\lambda)$ is the incident photon irradiance ($\text{E cm}^{-2}\text{s}^{-1}$), $\epsilon(\lambda)$ is the decadic molar absorption coefficient ($\text{M}^{-1}\text{cm}^{-1}$), $a(\lambda)$ is the solution absorbance, z is the solution depth in the Petri dish (cm), and $\Phi(\lambda)$ is the quantum yield (mol E^{-1}). For LP-UV photolysis, all the parameters were measured using the monochromatic light at 254 nm. When MP-UV lamp is used, all the parameters described in Eq (6) and (7) were integrated over the spectral distribution of the polychromatic light emitted by the source within the wavelength range of interest (200–320 nm), and the overall specific rate of light absorption was calculated as the sum of all values obtained in this wavelength range.

Table 1. Photochemical parameters of 36 TOxCs: molar absorption coefficient (ϵ), quantum yield (Φ), and UV dose-based rate constant (k'_d) during LP and MP-UV direct photolysis

Compound	LP-UV			MP-UV		
	$\epsilon_{254} (10^3, \text{M}^{-1}\text{cm}^{-1})$	$\Phi_{254} (10^{-2}, \text{mol}^{-1}\text{E}^{-1})$	$k'_d (\text{cm}^2\text{J}^{-1})^a$	$\epsilon_{200-320} (10^5, \text{M}^{-1}\text{cm}^{-1})^b$	$\Phi_{200-320} (10^{-2}, \text{mol}^{-1}\text{E}^{-1})$	$k'_d (\text{cm}^2\text{J}^{-1})^a$
Acesulfame (ASF)	3.6	18.7	-1.41	5.0	25.1	-1.19
Atenolol (ATN)	0.3	8.9	-0.06	2.9	7.4	-0.15
Atrazine (ATZ)	3.4	3.6	-0.26	10.9	5.9	-0.53
Benzophenone (BZP)	16.2	0.2	-0.06	10.2	0.4	-0.08
Benzotriazole (BTZ)	5.6	1.3	-0.13	5.5	5.5	-0.39
Bisphenol A (BSP)	1.0	5.6	-0.13	7.2	4.0	-0.24
Caffeine (CFN)	4.2	0.3	-0.03	8.3	0.7	-0.08
Carbamazepine (CBM)	5.5	0.2	-0.02	14.7	0.2	-0.03
Clofibric Acid (CFA)	0.3	46.7	-0.32	3.9	72.6	-2.10
Diclofenac (DCF)	6.1	22.2	-2.89	14.3	19.1	-3.28
Diethyltoluamide (DEET)	0.9	1.0	-0.02	4.8	1.3	-0.04
Diltiazem (DTZ)	7.5	1.2	-0.19	13.0	6.4	-0.83
Diphenhydramine (DPH)	0.3	12.1	-0.06	1.9	20.3	-0.30
Fluoxetine (FXT)	0.6	36.3	-0.45	4.4	57.0	-1.74
Gemfibrozil (GBZ)	0.5	6.7	-0.06	4.7	9.2	-0.34
Hydrochlorothiazide (HCT)	5.9	1.0	-0.13	13.5	2.9	-0.52
Hydrocortisone (HCS)	14.4	2.2	-0.71	7.4	4.5	-0.49
Ibuprofen (IBF)	0.3	3.5	-0.03	3.3	17.6	-0.38
Iohexol (IHX)	22.2	3.0	-1.41	16.6	3.2	-0.66
Iopamidol (IPML)	21.9	2.8	-1.29	16.6	4.1	-0.82
Iopromide (IPM)	22.6	2.8	-1.35	17.2	3.7	-0.78
Meprobamate (MPB)	0.1	17.0	-0.03	0.1	14.6	-0.02
Naproxen (NPX)	4.3	0.9	-0.06	18.6	10.3	-1.65
Prednisone (PNS)	13.1	6.9	-1.93	8.2	24.3	-3.28
Primidone (PMD)	0.2	11.6	-0.05	2.9	2.4	-0.04
Propranolol (PPN)	1.2	0.9	-0.03	13.3	2.5	-0.29
Propylparaben (PPB)	7.4	0.4	-0.06	10.9	0.2	-0.04
Simazine (SMZ)	0.6	21.7	-0.26	1.9	30.2	-0.49
Sucralose (SCL)	0.1	15.2	-0.04	0.3	15.5	-0.03
Sulfamethoxazole (SMZ)	16.5	5.8	-2.06	12.0	18.3	-2.29
Testosterone (TST)	14.9	2.2	-0.71	6.3	2.2	-0.22
Tris(1-chloro-2-propyl) phosphate (TCPP)	0.1	13.1	-0.03	0.3	13.5	-0.04
Tris(2-carboxyethyl) phosphine (TCEP)	0.1	9.4	-0.02	0.2	12.5	-0.03
Triclocarban (TCB)	4.1	3.0	-0.26	4.8	3.1	-0.28
Triclosan (TCS)	3.3	15.5	-1.09	14.2	17.0	-2.23
Trimethoprim (TMP)	2.9	0.6	-0.04	15.5	0.4	-0.04

^a k'_d is a slope of log removal (C/C_0) versus UV dose (J/cm^2)

$${}^b\varepsilon_{200-320} = \int_{200}^{320} \varepsilon(\nu) d\nu \quad (\nu: \text{wavelength})$$

In the photolytic degradation kinetics, both photochemical parameters such as molar absorption coefficient and quantum yield are wavelength dependent and most important to quantify the photon efficiency of a photochemical transformation of TOrCs (Wols et al., 2015). Since the photon energy of UV irradiation applied to the test water is assumed to be nearly constant, the degradation rate of a compound by UV direct photolysis is proportional to the photo-degradability that can be defined as the overall parameter of ϵ multiplied by Φ at each wavelength (Yu et al., 2015, Lester et al., 2014). It describes the overall sensitivity and vulnerability of a contaminant upon exposure to the UV light at the irradiation wavelength range used, therefore it can be used to characterize the photochemical response of TOrCs and reflect the effectiveness of UV irradiation for elimination of the photolabile compounds (Yu et al., 2015). The photo-degradability of each TOrCs with the paired photochemical parameters for LP- and MP-UV photolysis was shown in Fig. 2. Despite their relatively high absorbances of monochromatic light, the low quantum yields observed for iodinated contrast media (iohexol, iopamidol, and iopromide) are responsible for the low probability of being degraded using the absorbed photons (Fig. 2A). In contrast, acesulfame, which has the similar $Q\epsilon_{254}$ with iodinated contrasts, showed high transformation rate even with its low capacity of absorbing photons of the incident light. When exposed to polychromatic UV irradiation, the high absorbed light energy by triclosan may not be subsequently utilized in degrading the compound (Fig. 2B). Although comparable $Q\epsilon_{200-320}$ of triclosan was observed, fluoxetine led to high degree of photolysis with low photon absorption. Therefore, the photo-degradability considering both factors of molar absorption coefficient and quantum yield could be more useful in assessing the degradation of TOrCs by UV photolysis and its process efficiency.

A

B

Fig. 2. Correlation of molar absorption coefficient and quantum yield of TOxCs for (A) LP-UV and (B) MP-UV photolysis

3.2. Energy required to degrade TOrCs by direct LP- and MP-UV photolysis

In order to assess the process efficiency, the figures-of-merit can be used to compare UV-driven AOPs with respect to the electrical energy efficiency consumption associated with the contaminant removal, but also in sizing the UV equipment to generate the required electrical energy dose for specific treatment goals (Parsons, 2004). Electrical energy per order (EEO) is defined as the electrical energy in kilowatt hours (kWh) required to degrade a contaminant by one order of magnitude, that is 90% removal, in a unit volume (m^3). The EEO is based on the assumption that the contaminants are present in low concentration and follow pseudo first-order degradation kinetics. For a batch system, the EEO values can be determined from the following equation (Bolton et al., 2001):

$$\text{EEO} = \frac{P \times t \times 1000}{V \times 60 \times \log\left(\frac{C_0}{C}\right)} \quad \text{or} \quad \frac{6.396PU(\lambda)}{V\phi(\lambda)\varepsilon(\lambda)\ln(10)E_{\text{avg}}} \quad (\text{Eq. 8})$$

where P (kW) is the input electrical power to the lamp, t (min) is the irradiation time, V (L) is the volume of water treated and, C_0 and C (M) are the initial and final contaminant concentrations, respectively. E_{avg} is the average fluence rate in the UV reactor.

In order to provide a potential approach to compare UV photolysis with different types of UV lamp sources, electrical energies required to achieve 90% removal of the compounds by LP- and MP-UV direct photolysis are given in Fig. 3. The energy required for photo-degradation by one order of magnitude varies from one compound to another depending on molecular structure of TOrCs, ranging from 0.09 to 14.9 kWh m^{-3} (0.7 to 54.7 J cm^{-2}) and 0.09 to 11.8 kWh m^{-3} (0.3 to 46.0 J cm^{-2}) when mono- and polychromatic lights exposed, respectively. Smaller EEO values are more desirable, as they indicate a more efficacious process and consequently less electrical energy is required to achieve the treatment goal.

Since EEO is a function of the spectral radiant power over a specific wavelength range (254 nm for LP-UV lamp or 200–320 nm for MP-UV lamp) (Eq. 8), it depends on lamp spectrum and the fraction of light absorbed by the specific compound (Parsons, 2004). UV irradiation alone using

LP lamp is more effective at achieving degradation of most of the targeted TOrCs than MP lamp, but acesulfame, hydrocortisone, iohexol, iopamidol, iopromide, primidone, propylparaben, and testosterone. Compared to LP-UV lamp, the MP-UV lamp requires much higher electrical energy to generate a broad and continuous spectrum with the high intensity (Schalk et al.,2006). The benefit of high UV flux of MP-UV, however, is diminished by a far lower UV-C efficiency, resulting in higher energy consumption corresponding with the degradation capacity. Higher MP-UV lamp spectral outputs (the radiant output of a lamp versus wavelength) intensively emitting across the entire spectrum of UV-C range, it could thus ensure higher photo-degradability of TOrCs. In addition to the usual mercury lamps, the specialized UV lamps producing UV radiation at particular spectral lines for different purposes could be generated by florescent lamp, gas-discharge lamp, laser, and LED. Using the MP-UV lamp with an excellent UV-C efficiency and a much higher power density than traditional lamp, EEO could be significantly reduced to effectively degrade the TOrCs for the practical application of UV AOP in WWTPs.

Fig. 3. Comparison of EEO for TOrCs removal by LP and MP-UV direct photolysis (The asterisks (*) indicate the compounds with larger E_{EO} required for MP-UV photolysis).

As mentioned above, the photolytic degradation kinetics of TOrCs by the exposure of UV irradiation are govern by the paired photochemical parameters of molar absorption coefficients and quantum yield. Consequently, EEO or UV dose required for 90% removal of TOrCs is thus inversely proportional to the photo-degradability ($\Phi_{\epsilon_{254}}$ for LP-UV and $\Phi_{\epsilon_{200-320}}$ for MP-UV) of the target contaminant over the emission spectrum of the lamps (Fig. 4), but not solely correlated with either single factor of molar absorption coefficients or quantum yield (Fig. S4 and S5). The contour lines for a function of two variables such as molar absorption coefficients and quantum yield are displayed the curves connecting along which the function has a constant value of photo-degradability in response to LP- and MP-UV lights (Fig. 2). The comparable EEO (0.18 kWh m^{-3}) or UV dose (0.7 J cm^{-2}) required to degrade acesulfame and iodinated contrast media (iohexol,

iopamidol, and iopromide) were observed along the isolines in a given photo-degradability using LP-UV lamp, but representing different levels of photochemical properties (ϵ_{254} and Φ_{254}) (Fig. 2A and Fig. S2). During MP-UV photolysis, the considerably photolabile TOxCs such as sulfamethoxazole, diclofenac, and prednisone required only 0.09 kWh m⁻³ and 0.3 J cm⁻² with different photochemical properties, but displaying at the same photo-degradability contour line (Fig. 2B and Fig. S3).

A

B

Fig. 4. Correlation of EEO and photo-degradability (absorption coefficient (ϵ) $\times$ quantum yield (Φ)) of TOrCs for (a) LP-UV and (b) MP-UV photolysis

Considering the photo-degradability of each TOrCs, the compounds were practically divided into three groups according to their vulnerability to direct UV photolysis such as group 1 (UV dose < 1 J cm⁻²), group 2 (1 J cm⁻² < UV dose < 10 J cm⁻²), and group 3 (10 J cm⁻² < UV dose < 100 J cm⁻²) for further framework of determining the appropriate an indicator compound to assess the process performance during UV-based AOP system, as shown in Fig. S2 and S3. For LP-UV photolysis, the group 1 includes the photo-susceptible TOrCs (diclofenac, prednisone, sulfamethoxazole, acesulfame, iohexol, iopromide, iopamidol and triclosan); the compounds with relatively moderate amenability to direct photolysis are categorized into group 2 (testosterone, hydrocortisone, fluoxetine, clofibric acid, simazine, atrazine, triclocarban, diltiazem, benzotriazole, hydrochlorothiazide, and bisphenol A); and the group 3 consists of the photo-resistant TOrCs (diphenhydramine, naproxen, gemfibrozil, propylparaben, primidone, atenolol, benzophenone, sucralose, trimethoprim, caffeine, TCP, ibuprofen, propranolol, meprobamate, carbamazepine,

DEET, and TCEP). For MP-UV photolysis, the group 1 includes the photo-susceptible TOrCs (prednisone, diclofenac, sulfamethoxazole, triclosan, clofibric acid, fluoxetine, naproxen, and acesulfame); the TOrCs in group 2 showed relatively moderate amenability to direct photolysis (diltiazem, iopamidol, iopromide, iohexol, atrazine, hydrochlorothiazide, simazine, hydrocortisone, ibuprofen, benzotriazole, gemfibrozil, propranolol, diphenhydramine, triclocarban, testosterone, bisphenol A, and atenolol); the group 3 consists of the photo-resistant TOrCs (benzophenone, caffeine, DEET, trimethoprim, sucralose, primidone, TCP, propylparaben, carbamazepine, TCEP, and meprobamate)

Because the EEO for a flow-through reactor can be also expressed as a function of the UV dose delivered in the reactor, scale up from CBD or bench testing to full-scale could be translated using this framework and guidelines to predict the photochemical kinetics and destruction of TOrCs. Unlike CBD, however, the UV dose delivered to the water in the flow-through UV reactor is dependent on the optics (UV lamp, reactor housing, quartz sleeves and ballasts) and hydraulics (lamp configuration and orientation, flowrate and water transmittance). Using Computational Fluid Dynamic modeling (CFD) and UV radiation models which account for the flow patterns and the UV radiation distribution, the UV dose delivered and EEO for full-scale UV system could be determined.

3.3. Proposed ranking system for selection of potential indicator compounds

A comprehensive ranking system was developed to help water utilities to rank the suitable indicator compound of TOrCs for monitoring and assessing the treatment efficiency of UV AOPs for a potable water reuse system, using mainly two criteria: (1) occurrence of TOrCs in wastewater treatment plants (WWTPs) effluents including detection frequency (DF), detection ratio (DR), and activated sludge removal, and (2) photochemical parameters such as photo-degradability and

rate constant of hydroxyl radical ($\bullet\text{OH}$) oxidation ($k_{\bullet\text{OH}}$) during LP (Table S3) and MP-UV AOPs (Table S4).

3.3.1. Occurrence of TOrCs in WWTPs effluents

Numerous studies have been reported the presence of TOrCs in effluents of conventional wastewater treatment facilities in many countries (Dickenson et al., 2011, Loos et al., 2013). To be viable indicator candidates for monitoring efforts to assess the attenuation of TOrCs by UV AOPs, the compounds occur at concentrations significantly above their detection limits and at high frequencies in multiple WWTPs.

A suitable indicator compound is one that can be considerably quantified changes in concentration that occur in WWTPs effluents and attenuation through the UV-driven processes. It is thus necessary that analytical methods exist for targeted compounds and have been applied to measure these compounds in treated wastewater. However, it is difficult to detect the loss of a compound, if it is initially present at a low concentration near the detection limit. Therefore, it is necessary to consider the concentration of each TOrCs relative to the limit of quantification (LOQ) (Dickenson et al., 2011). DR can be used for a compound in a given study based on the reported median concentration divided by the LOQ (Sedlak et al., 2004), and the values were represented in Table S3 and S4.

Along with a compound needing to be easily detected it is also necessary to be frequently detected in order to be a potential indicator compound. The average DF across studies was listed for identified indicator compounds (Table S3 and S4). It is noteworthy that the DF is biased through the consideration of the number of WWTPs that was reported, and which can vary with region, per-capita water consumption (resulting in different levels of dilution) and usage patterns (Dickenson et al., 2011).

3.3.2. Photochemical parameters of TOrCs during UV AOPs

Besides the occurrence level of TOrCs in the treated effluents as primary criteria, the screening approach developed in this study utilizes the subsequent criteria using the unique photochemical properties of a compound such as photo-degradability ($\Phi_{\epsilon\lambda}$) and radical oxidation ($k_{\bullet\text{OH}}$) to assess attenuation and fate of TOrCs in the effluents treated through the UV AOPs. Based on the vulnerability to direct UV photolysis, photo-susceptible, moderate photo-degradable, and photo-resistant indicator compounds were categorized into three groups, as shown in Fig. 5, Table S3 and S4. Removal of the compounds included in group 2 and 3 is not likely to be feasible due to its low photo-degradability ($\Phi_{\epsilon\lambda}$) and high demand of energy, while UV AOPs (i.e., UV/H₂O₂) will considerably increase the transformation by addition of oxidants to allow for $\bullet\text{OH}$ radical-mediated pathway (Yu et al., 2015). The purpose of the categorization of TOrCs in Section 2 was to help water utilities to conduct category-specific monitoring for assessing the attenuation of the compounds and process efficiency when operating either LP or MP-UV AOPs.

A

B

Fig. 5. Ranking system of TOrCs for selecting indicator compound to assess process performance of (A) LP-UV AOP and (B) MP-UV AOP

3.3.3. Ranking system for selecting indicator compounds of TOrCs for UV AOPs

A summary of the ranking approaches is presented to assess the process efficiency with respect to the attenuation of TOrCs by LP-UV (Fig. 5A) and MP-UV (Fig. 5B) AOPs. In developing a ranking system to select prioritized TOrCs for tailoring monitoring program, both important criteria factors are considered such as (1) the occurrence level of TOrCs in secondary-treated wastewater as a source for potable water reuse and (2) the photochemical properties governing the constituent's transformation. The use of multiple criteria would allow characterization of TOrCs behavior in each group through the treatment of UV AOPs and prioritization of the rank of indicator markers to be monitored (Table S2).

Rank scores of TOrCs were calculated as summations of multiplications of importance weights and utility functions of multiple criteria (Kumar and Xagorarakis, 2010). An expression for calculating an overall rank score (S_{overall}) of indicator compounds can be written as:

$$S_{\text{overall}} = W_1 \cdot S_{\text{DF}} + S_{\text{DR}} + S_{\text{AS}} + W_2(S_{\Phi\epsilon} + S_{k\cdot\text{OH}}) \quad (\text{Eq. 9})$$

where S_{DF} , S_{DR} , S_{AS} represent the criteria-based scores according to occurrence level of TOrCs in the secondary effluents such as detection frequency (DF), detection ratio (DR), and activated sludge removal (AS), $S_{\Phi\epsilon}$ and $S_{k\cdot\text{OH}}$ denote the criteria-based scores of photo-degradability and $\cdot\text{OH}$ oxidation, and W is an importance weight of criteria for DF (W_1) and photochemical parameters (W_2).

The scores awarded between 1 and 3 points to each TOrCs in the criteria based on the occurrence in WWTPs effluents and photochemical parameters for LP- and MP-UV AOP (Table S2). Due to the nature of equation used for calculating overall rank score, the overall rank score of each TOrCs varies between 6.1 and 21 (Eq. 9). Higher scores are more desirable, as they indicate a more suitable indicator marker to compare the relative efficiency of UV direct photolysis with UV AOPs, subsequently optimizing their processes.

The selected TOrCs were classified into three groups that served as indicator compounds: (1) Group 1 includes the photolabile TOrCs which are easily degraded with no oxidants added when exposed to either LP or MP UV lights. In this category, the compounds with higher scores describe a suitable indicator for assessing the attenuation of TOrCs by UV direct photolysis. Acesulfame, diclofenac, and sulfamethoxazole would be good indicators in response to both LP and MP-UV photolysis. (2) Group 2 consists of the moderate photo-degradable compounds with high reactivity of $\cdot\text{OH}$ oxidation, and which can be used as markers for evaluating the treatment efficiency of both photolysis and radical-mediated reaction. Benzotriazole, fluoxetine, and hydrochlorothiazide ranked high on the successful indicator compounds for assessing LP-UV AOP, while propranolol, diltiazem, and diphenhydramine can be considered for MP-UV AOP. (3) Group 3 is composed of the recalcitrant TOrCs by photolysis, but highly reactive with $\cdot\text{OH}$ radicals. The compounds in this

group are mainly decomposed by $\bullet\text{OH}$ radicals, therefore the overall rank scores little appreciate the effects of direct photolysis. Carbamazepine and DEET would be good candidates with highest priority during both LP and MP-UV AOP.

Therefore, this proposed ranking system is expected to provide water utilities with a comprehensive tool for developing a priority list of TOrCs to assess the treatment efficiency through UV AOPs. In addition, it could be utilized as a monitoring program framework for any utility that has the different trends of TOrCs occurrence from this study when UV AOP systems are intended to attenuate TOrCs.

4. Conclusions

In this study, the ranking system was first proposed to select a viable indicator compound that represent the different photochemical groups depending on their relative reactivity to UV direct photolysis and $\bullet\text{OH}$ oxidation, and which can be used to evaluate the attenuation efficiency of TOrCs and process performance during LP and MP-UV AOP treatment of reclaimed water. The photolysis kinetic parameters and electrical energy required to efficiently degrade TOrCs by UV irradiation alone presented in this study can assist in selecting contaminants of defined groups and achieving a treatment goal through AOP system. The compounds ranked high in the developed priority list in each group can be used a representative indicator compound to assess attenuation of similar reactive TOrCs that are of interest to the researchers or agencies who initiated the monitoring system for employing UV AOP system to optimize their processes. Furthermore, based on the site-specific occurrence profile of wastewater effluents and the UV system, the proposed ranking system could be utilized to provide operators with the customized tool to predict process performance, and which needs to be taken into consideration when making operational decisions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found.

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Fig. 1. Overlaid molar absorption coefficient of all TOCs and spectral output of LP and MP-UV lamps evaluated in this study

A

B

Fig. 2. Correlation of molar absorption coefficient and quantum yield of TOxTs for (A) LP-UV and (B) MP-UV photolysis

Fig. 3. Comparison of EEO for TORCs removal by LP and MP-UV direct photolysis (The asterisks (*) indicate the compounds with larger EEO required for MP-UV photolysis).

A

B

Fig. 4. Correlation of EEO and photo-degradability (absorption coefficient (ϵ) $\times$ quantum yield (Φ)) of TOxCs for (a) LP-UV and (b) MP-UV photolysis

A

B

Fig. 5. Ranking system of TORCs for selecting indicator compound to assess process performance of (A)

LP-UV AOP and (B) MP-UV AOP

Table 1. Photochemical parameters of 36 TOrcs: molar absorption coefficient (ϵ), quantum yield (Φ), and UV dose-based rate constant (k'_d) during LP and MP-UV direct photolysis

Compound	LP-UV			MP-UV		
	$\epsilon_{254} (10^3, \text{M}^{-1}\text{cm}^{-1})$	$\Phi_{254} (10^{-2}, \text{mol}^{-1}\text{E}^{-1})$	$k'_d (\text{cm}^2\text{J}^{-1})^a$	$\epsilon_{200-320} (10^5, \text{M}^{-1}\text{cm}^{-1})^b$	$\Phi_{200-320} (10^{-2}, \text{mol}^{-1}\text{E}^{-1})$	$k'_d (\text{cm}^2\text{J}^{-1})^a$
Acesulfame (ASF)	3.6	18.7	-1.41	5.0	25.1	-1.19
Atenolol (ATN)	0.3	8.9	-0.06	2.9	7.4	-0.15
Atrazine (ATZ)	3.4	3.6	-0.26	10.9	5.9	-0.53
Benzophenone (BZP)	16.2	0.2	-0.06	10.2	0.4	-0.08
Benzotriazole (BTZ)	5.6	1.3	-0.13	5.5	5.5	-0.39
Bisphenol A (BSP)	1.0	5.6	-0.13	7.2	4.0	-0.24
Caffeine (CFN)	4.2	0.3	-0.03	8.3	0.7	-0.08
Carbamazepine (CBM)	5.5	0.2	-0.02	14.7	0.2	-0.03
Clofibric Acid (CFA)	0.3	46.7	-0.32	3.9	72.6	-2.10
Diclofenac (DCF)	6.1	22.2	-2.89	14.3	19.1	-3.28
Diethyltoluamide (DEET)	0.9	1.0	-0.02	4.8	1.3	-0.04
Diltiazem (DTZ)	7.5	1.2	-0.19	13.0	6.4	-0.83
Diphenhydramine (DPH)	0.3	12.1	-0.06	1.9	20.3	-0.30
Fluoxetine (FXT)	0.6	36.3	-0.45	4.4	57.0	-1.74
Gemfibrozil (GBZ)	0.5	6.7	-0.06	4.7	9.2	-0.34
Hydrochlorothiazide (HCT)	5.9	1.0	-0.13	13.5	2.9	-0.52
Hydrocortisone (HCS)	14.4	2.2	-0.71	7.4	4.5	-0.49
Ibuprofen (IBF)	0.3	3.5	-0.03	3.3	17.6	-0.38
Iohexol (IHx)	22.2	3.0	-1.41	16.6	3.2	-0.66
Iopamidol (IPML)	21.9	2.8	-1.29	16.6	4.1	-0.82
Iopromide (IPM)	22.6	2.8	-1.35	17.2	3.7	-0.78
Meprobamate (MPB)	0.1	17.0	-0.03	0.1	14.6	-0.02
Naproxen (NPX)	4.3	0.9	-0.06	18.6	10.3	-1.65
Prednisone (PNS)	13.1	6.9	-1.93	8.2	24.3	-3.28
Primidone (PMD)	0.2	11.6	-0.05	2.9	2.4	-0.04
Propranolol (PPN)	1.2	0.9	-0.03	13.3	2.5	-0.29
Propylparaben (PPB)	7.4	0.4	-0.06	10.9	0.2	-0.04
Simazine (SMZ)	0.6	21.7	-0.26	1.9	30.2	-0.49
Sucralose (SCL)	0.1	15.2	-0.04	0.3	15.5	-0.03
Sulfamethoxazole (SMZ)	16.5	5.8	-2.06	12.0	18.3	-2.29
Testosterone (TST)	14.9	2.2	-0.71	6.3	2.2	-0.22
Tris(1-chloro-2-propyl) phosphate (TCPP)	0.1	13.1	-0.03	0.3	13.5	-0.04
Tris(2-carboxyethyl) phosphine (TCEP)	0.1	9.4	-0.02	0.2	12.5	-0.03
Triclocarban (TCB)	4.1	3.0	-0.26	4.8	3.1	-0.28
Triclosan (TCS)	3.3	15.5	-1.09	14.2	17.0	-2.23
Trimethoprim (TMP)	2.9	0.6	-0.04	15.5	0.4	-0.04

^a k'_d is a slope of log removal (C/C_0) versus UV dose (J/cm^2)

^b $\epsilon_{200-320} = \int_{200}^{320} \epsilon(\nu) d\nu$ (ν : wavelength)

Highlights

- A ranking system for monitoring TOrC indicators for UV AOPs was developed
- Indicator TOrCs are prioritized by occurrence and photochemical reactivity.
- Both direct photolysis and OH radical oxidation rates are evaluated for UV AOPs.
- Indicator monitoring successfully predicts broader treatment efficacy of UV AOPs.

Supplementary data

Strategies for selecting indicator compounds to assess attenuation of emerging contaminants during UV advanced oxidation process

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Pages 9

Table 1 (Table S1)

Fig. 6 (Fig. S1 – S6)

Supplementary data

SI 1. Analysis of TOrCs using triple quadrupole LC-MS/MS

Table S1. Class and use of 36 TOrCs analyzed in this study with their limit of detection (LOD) for quantification by LC-MS/MS method

Table S2. Score criteria based on (a) occurrence in WWTPs and photochemical parameters for (b) LP-UV AOP and (c) MP-UV AOP

Table S3. Ranking system of TOrCs for selecting indicator compound and assessing process performance during LP-UV AOP

Table S4. Ranking system of TOrCs for selecting indicator compound and assessing process performance during MP-UV AOP

Fig. S1. Molar absorption coefficients of TOrCs in the wavelength range of 200–320 nm with spectral sensitivity of LP and MP-UV lamp used in this study

Fig. S2. (a) EEO and (b) UV dose required to achieve 90% removal using LP-UV photolysis

Fig. S3. (a) EEO and (b) UV dose required to achieve 90% removal using MP-UV photolysis

Fig. S4. Correlation of EEO and UV dose required to achieve 90% removal for TOrCs with either (a) molar absorption coefficient or (b) quantum yield during LP-UV photolysis

Fig. S5. Correlation of EEO and UV dose required to achieve 90% removal for TOrCs with either (a) molar absorption coefficient or (b) quantum yield during MP-UV photolysis

Fig. S6. Scores for selection of indicator TOrCs in each group to evaluate the performance of (a) LP-UV AOP and (b) MP-UV AOP

SI 1. Analysis of TOrCs using triple quadrupole LC-MS/MS

All analytical standards used in this study were >97% purity and purchased from Sigma Aldrich (St. Louis, MO), Alfa Aesar (Ward Hill, MA), or US Pharmacopeia (Washington, DC). The isotopically labeled surrogate standards were procured from Cambridge Isotope Laboratories (Andover, MA) except meprobamate-d₃, triclocarban-¹³C₆ and ¹³C₆-diclofenac from Toronto Research Chemicals (Ontario, Canada); iopromidol-d-3 from Santa Cruz Biotechnology (Dallas, TX); gemfibrozil-d₆, and diphenhydramine-d₅ from C/D/N Isotopes (Quebec, Canada). Acetonitrile (ACN; HPLC grade), methanol (HPLC grade), acetic acid (ACS grade), formic acid (LC/MS grade), and ammonium acetate (ACS grade) were purchased from Fisher Scientific (Pittsburgh, PA), while HPLC grade water was purchased from Burdick & Jackson (Muskegon, MI).

The optimized analytical methods were performed by liquid chromatography tandem mass spectrometry (LC–MS/MS) following two different sample preparation steps: (1) on-line solid-phase extraction (SPE); and (2) direct injection without enrichment and extraction.

A fully automated on-line SPE directly coupled to LC–MS/MS was used for analysis of 31 TOrCs in the water samples, which allows for integration of sample clean-up, extraction and analysis. The 5 mL aliquot sample was spiked with a mixture of all isotope-labeled surrogates to achieve a final concentration of 200 ng L⁻¹, and then filtered through 0.2-μm Captiva PES syringe filters (Agilent Technologies) prior to analysis. Automated pre-concentration of all samples was performed using an Agilent flexible cube (FlexCube) module coupled to an auto sampler with a programmable multi-draw capacity. An Agilent 1290 Infinity Ultra High Performance Liquid Chromatography (UHPLC) binary pump with Agilent Poroshell 120 ECC-18 (2.1 mm × 50 mm, 2.7 mm) column was used for chromatographic separation of the selected TOrCs. Mass spectrometry was performed on an Agilent 6460 triple quadrupole mass spectrometer, and run in dynamic multiple reaction monitoring (DMRM) mode, with fast polarity switching for simultaneous analysis in ESI positive and negative mode. Data acquisition and analysis was performed using Agilent MassHunter software.

Due to their high concentrations in wastewater, the monitoring of 5 TOrCs (acesulfame, iohexol, iopamidol, iopromide and sucralose) was carried out by direct injection coupled to LC–MS/MS, also referred to as Large Volume Injection (LVI) LC/MS-MS. After spiking a surrogate standard mix to achieve a final concentration of 200 μg L⁻¹, the sample was filtered through 0.2-μm Captiva PES syringe filters (Agilent). The analysis of water samples was performed on an Agilent 1260

Infinity HPLC, coupled to an Agilent 6490 Triple Quadrupole LC/MS using both positive and negative ESI. After multiple reaction monitoring (MRM) transitions for the analytes and their surrogate standards, the target compounds were identified and quantified using Agilent MassHunter software.

Table S1. Class and use of 36 TOrCs analyzed in this study with their limit of detection (LOD) for quantification by LC-MS/MS method

Analyte	Use	Class	LOD (ng/L)
Acesulfame	Artificial sweetener	Industrial compound	10
Atenolol	β -Blocker	Pharmaceutical	1
Atrazine	Herbicide	Pesticide	0.2
Benzophenone	UV blocker	Personal care product	5
Benzotriazole	Corrosion inhibitor	Industrial compound	10
Bisphenol A	Plasticizer	Industrial compound	10
Caffeine	Stimulant	Personal care product	0.2
Carbamazepine	Anti-seizure	Pharmaceutical	0.1
Clofibric acid	Lipid regulator metabolite	Pharmaceutical	0.2
DEET	Insect repellent	Personal care product	0.1
Diclofenac	Anti-arthritic	Pharmaceutical	2
Diphenhydramine	Anti-arrhythmic	Pharmaceutical	0.5
Diltiazem	Anti-histamine	Pharmaceutical	0.1
Fluoxetine	Anti-depressant	Pharmaceutical	1
Gemfibrozil	Anti-cholesterol	Pharmaceutical	0.2
Hydrocortisone	Anti-inflammatory glucocorticoid	Hormone	5
Hydrochlorothiazide	Anti-hypertensive	Pharmaceutical	0.2
Ibuprofen	Analgesic	Pharmaceutical	0.5
Iohexol	X-ray contrast media	Pharmaceutical	100
Iopamidol	X-ray contrast media	Pharmaceutical	50
Iopromide	X-ray contrast media	Pharmaceutical	100
Meprobamate	Anti-anxiety	Pharmaceutical	0.2
Naproxen	Analgesic	Pharmaceutical	1
Prednisone	Anti-inflammatory	Pharmaceutical	1
Primidone	Anti-convulsant	Pharmaceutical	0.5
Propranolol	β -Blocker	Pharmaceutical	1
Propylparaben	Preservative in cosmetics	Personal care product	1
Simazine	Herbicide	Pesticide	0.2
Sucralose	Artificial sweetener	Industrial compound	75
Sulfamethoxazole	Antibiotic	Pharmaceutical	0.2
TCEP	Flame retardant	Personal care product	1
TCPP	Flame retardant	Personal care product	5
Testosterone	Androgen	Hormone	2.5
Triclocarban	Antibiotic	Personal care product	0.5
Triclosan	Anti-microbial	Personal care product	1
Trimethoprim	Antibiotic	Pharmaceutical	0.1

Table S2. Score criteria based on (a) occurrence in WWTPs and photochemical parameters for (b) LP-UV AOP and (c) MP-UV AOP

(a)

Score	DF (%) ^a	DR	Activated sludge removal (%)
3	70-100	> 500	0-40
2	40-70	100-500	40-70
1	0-40	1-100	70-100

^a Weight: 1 (>50 WWTPs), 0.5 (10-50 WWTPs), 0.1 (1-10 WWTPs)

(b)

LP-UV Score ^a	Group 1		Group 2		Group 3	
	$\Phi\epsilon_{254}$ ^b	k_{OH} ^c	$\Phi\epsilon_{254}$	k_{OH}	$\Phi\epsilon_{254}$	k_{OH}
3	> 900	1 – 5	400 – 500	> 10	0 – 10	> 10
2	700 – 900	5 – 10	200 – 400	5 – 10	10 – 30	5 – 10
1	500 – 700	> 10	50 – 200	1 – 5	30 – 50	1 – 5

^a Weight: 2 for UV AOP parameters ($Q_{\epsilon_{254}}$ for photolysis and k_{OH} for $\bullet OH$ oxidation)

^b $\Phi\epsilon_{254}$: Φ_{254} ($\text{mol}^{-1}\text{E}^{-1}$) $\times$ ϵ_{254} ($\text{M}^{-1}\text{cm}^{-1}$)

^c k_{OH} : $\times 10^9 \text{ M}^{-1}\text{s}^{-1}$

(c)

MP-UV Score ^a	Group 1		Group 2		Group 3	
	$\Phi\epsilon_{200-320}$ (10^3) ^b	k_{OH} ^c	$\Phi\epsilon_{200-320}$ (10^3)	k_{OH}	$\Phi\epsilon_{200-320}$ (10^3)	k_{OH}
3	250 – 300	1 – 5	70 – 100	> 10	0 – 4	> 10
2	200 – 250	5 – 10	40 – 70	5 – 10	4 – 7	5 – 10
1	100 – 200	> 10	10 – 40	1 – 5	7 – 10	1 – 5

^a Weight: 2 for UV AOP parameters ($Q_{\epsilon_{200-320}}$ for photolysis and k_{OH} for $\bullet OH$ oxidation)

^b $\Phi\epsilon_{200-320}$: $\Phi_{200-320}$ ($\text{mol}^{-1}\text{E}^{-1}$) $\times$ $\epsilon_{200-320}$ ($\text{M}^{-1}\text{cm}^{-1}$)

^c k_{OH} : $\times 10^9 \text{ M}^{-1}\text{s}^{-1}$

Table S3. Ranking system of TOrCs for selecting indicator compound and assessing process performance during LP-UV AOP

Rank	Compound	Occurrence in WWTP effluent ^a				Photo-chemical parameter		Score					
		#Total WWTPs	DF (%)	DR	Activated sludge removal (%)	Φ _{E254}	k _{·OH} (10 ⁹) ^b	DF (%)	DR	Activated sludge removal (%)	Φ _{E254}	k _{·OH}	Total
Group 1 (Photo-susceptible TOrCs)													
1	Acesulfame	90	93	1430	0 (n=10)	670	4	3	3	3	2	6	17.0
2	Diclofenac	90	89	43	53 (n=37)	1365	8	3	1	2	6	4	16.0
3	Sulfamethoxazole	90	83	8	56 (n=17)	966	6	3	1	2	6	4	16.0
4	Iopamidol	90	15	3	17 (n=1)	603	3	1	1	3	2	6	13.0
5	Iopromide	90	36	54	69 (n=3)	624	3	1	1	2	2	6	12.0
6	Iohexol	90	18	3	89 (n=1)	670	4	1	1	1	2	6	11.0
7	Triclosan	4	100	79	91 (n=30)	516	6	0.3	1	1	2	4	8.3
8	Prednisone	7	4	15	99 (n=28)	900	NA ^c	0.1	1	1	4	0	6.1
Group 2 (Moderate photo-degradable TOrCs)													
1	Benzotriazole	90	97	68	75 (n=14)	74	11	3	1	1	2	6	13.0
2	Fluoxetine	90	22	0.4	46 (n=3)	220	9	1	1	2	4	4	12.0
3	Hydrochlorothiazide	5	98	1533	52.5 (n=1)	61	6	0.3	3	2	2	4	11.3
4	Hydrocortisone	7	100	3	98 (n=28)	322	8	0.3	1	1	4	4	10.3
5	Triclocarban	6	92	3	97 (n=1)	125	10	0.3	1	1	2	6	10.3
6	Clofibric Acid	90	26	3	43 (n=3)	159	5	1	1	2	2	4	10.0
7	Atrazine	90	68	2	13 (n=5)	123	2	2	1	3	2	2	10.0
8	Diltiazem	90	79	13	27 (n=6)	92	NA	3	1	3	2	0	9.0
9	Bisphenol A	4	100	9	80 (n=49)	56	8	0.3	1	1	2	4	8.3
10	Simazine	90	28	5	90 (n=5)	138	3	1	1.0	1	2	2	7.0
11	Testosterone	4	75	20	86 (n=8)	332	NA	0.3	1	1	4	0	6.3
Group 3 (Photo-resistant TOrCs)													

1	Carbamazepine	90	90	752	24 (n=10)	10	8	3	3	3	6	4	19.0
2	DEET	90	100	196	58 (n=8)	10	5	3	2	2	6	4	17.0
3	Propranolol	25	79	130	43 (n=3)	11	11	1.5	2	2	4	6	15.5
4	Trimethoprim	90	93	18	60 (n=10)	18	6	3	1	2	4	4	14.0
5	Atenolol	4	100	880	53 (n=10)	28	7	0.3	3	2	4	4	13.3
6	Diphenhydramine	90	98	98	37 (n=6)	41	5.4	3	1	3	2	4	13.0
7	Sucralose	90	88	17	0 (n=10)	18	2	3	1	3	4	2	13.0
8	TCP	90	100	620	0 (n=2)	14	0	3	3	3	4	0	13.0
9	Caffeine	90	93	7	95 (n=12)	13	6	3	1	1	4	4	13.0
10	TCEP	90	100	71	0 (n=2)	9	0.6	3	1	3	6	0	13.0
11	Primidone	5	100	32	39 (n=9)	25	7	0.3	1	3	4	4	12.3
12	Ibuprofen	90	57	4	92 (n=50)	12	7	2	1	1	4	4	12.0
13	Meprobamate	4	100	140	11 (n=1)	11	4	0.3	2	3	4	2	11.3
14	Propylparaben	6	83	20	95 (n=3)	30	5	0.3	1	1	4	4	10.3
15	Gemfibrozil	90	60	5	81 (n=16)	33	7	2	1	1	2	4	10.0
16	Naproxene	4	5	460	88 (n=26)	41	9	0.1	2	1	2	4	9.1
17	Benzophenone	4	100	17	87 (n=8)	37	9	0.3	1	1	2	4	8.3

^a (Deblonde et al., 2011, Dickenson et al., 2011, Loos et al., 2013)

^b (Kim et al., 2009, Lopez et al., 2003, Tian et al., 2014, Wang et al., 2012)

^c NA (Not available)

Table S4. Ranking system of TOrCs for selecting indicator compound and assessing process performance during MP-UV AOP

Rank	Compound	Occurrence in WWTP effluent ^a				Photochemical parameter		Score					
		#Total WWTPs	DF (%)	DR	Activated sludge removal (%)	Φ _{E₂₀₀₋₃₂₀} (10 ³)	k _{·OH} (10 ⁹) _b	DF (%)	DR	Activated sludge removal (%)	Φ _{E₂₀₀₋₃₂₀}	k _{·OH}	Total
Group 1 (Photo-susceptible TOrCs)													
1	Acesulfame	90	93	1430	0 (n=10)	127	4	3	3	3	2	6	17.0
2	Diclofenac	90	89	43	53 (n=37)	273	8	3	1	2	6	4	16.0
3	Clofibric Acid	90	26	3	43 (n=3)	282	5	1	1	2	6	4	14.0
4	Sulfamethoxazole	90	83	8	56 (n=17)	219	6	3	1	2	4	4	14.0
5	Fluoxetine	90	22	0.4	46 (n=3)	249	9	1	1	2	4	4	12.0
6	Triclosan	4	100	79	91 (n=30)	242	6	0.3	1	1	4	4	10.3
7	Naproxen	4	5	460	88 (n=26)	191	9	0.1	2	1	2	4	9.1
8	Prednisone	7	4	15	99 (n=28)	198	NA ^c	0.1	1	1	2		4.1
Group 2 (Moderate photo-degradable TOrCs)													
1	Propranolol	25	79	130	43 (n=3)	33	11	1.5	2	2	2	6	13.5
2	Diltiazem	90	79	13	27 (n=6)	83	NA	3	1	3	6	0	13.0
3	Diphenhydramine	90	98	98	37 (n=6)	38	5	3	1	3	2	4	13.0
4	Benzotriazole	90	97	68	75 (n=14)	30	11	3	1	1	2	6	13.0
5	Atrazine	90	68	2	13 (n=5)	65	2	2	1	3	4	2	12.0
6	Ibuprofen	90	57	4	92 (n=50)	59	7	2	1	1	4	4	12.0
7	Gemfibrozil	90	60	5	81 (n=16)	43	7	2	1.0	1	4	4	12.0
8	Hydrochlorothiazide	5	98	1533	52.5 (n=1)	39	6	0.3	3	2	2	4	11.3
9	Atenolol	4	100	880	53 (n=10)	21	7	0.3	3	2	2	4	11.3
10	Iopamidol	90	15	3	17 (n=1)	67	3	1	1	3	4	2	11.0
11	Triclocarban	6	92	3	97 (n=1)	15	10	0.3	1	1	2	6	10.3
12	Iopromide	90	36	54	69 (n=3)	63	3	1	1	2	4	2	10.0

13	Simazine	90	28	5	90 (n=5)	58	3	1	1	1	4	2	9.0
14	Iohexol	90	18	3	89 (n=1)	53	4	1	1	1	4	2	9.0
15	Hydrocortisone	7	100	3	98 (n=28)	33	8	0.3	1	1	2	4	8.3
16	Bisphenol A	4	100	9	80 (n=49)	29	8	0.3	1	1	2	4	8.3
17	Testosterone	4	75	20	86 (n=8)	14	NA	0.3	1	1	2	0	4.3

Group 3 (Photo-resistant TORCs)

1	Carbamazepine	90	90	752	24 (n=10)	3	8	3	3	3	6	4	19.0
2	DEET	90	100	196	58 (n=8)	6	5	3	2	2	4	4	15.0
3	Trimethoprim	90	93	18	60 (n=10)	6	6	3	1	2	4	4	14.0
4	Meprobamate	4	100	140	11 (n=1)	2	4	0.3	2	3	6	2	13.3
5	Caffeine	90	93	7	95 (n=12)	6	6	3	1	1	4	4	13.0
6	TCP	90	100	620	0 (n=2)	5	0.2	3	3	3	4	0	13.0
7	Sucralose	90	88	17	0 (n=10)	4	2	3	1	3	4	2	13.0
8	TCEP	90	100	71	0 (n=2)	3	0.6	3	1	3	6	0	13.0
9	Primidone	5	100	32	39 (n=9)	7	7	0.3	1	3	4	4	12.3
10	Propylparaben	6	83	20	95 (n=3)	2	5	0.3	1	1	6	4	12.3
11	Benzophenone	4	100	17	87 (n=8)	5	9	0.3	1	1	4	4	10.3

^a (Deblonde et al., 2011, Dickenson et al., 2011, Loos et al., 2013)

^b (Kim et al., 2009, Lopez et al., 2003, Tian et al., 2014, Wang et al., 2012)

^c NA (Not available)

Fig. S1. Molar absorption coefficients of TOrCs in the wavelength range of 200–320 nm with spectral sensitivity of LP and MP-UV lamp used in this study

3 (a)

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6 (b)

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8 Fig. S2. (a) EEO and (b) UV dose required to achieve 90% removal using LP-UV photolysis

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10 (a)

11

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13 (b)

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16 Fig. S3. (a) EEO and (b) UV dose required to achieve 90% removal using MP-UV photolysis

17 (a)

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19

20 (b)

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22

23 Fig. S4. Correlation of EEO and UV dose required to achieve 90% removal for TORCs with
 24 either (a) molar absorption coefficient or (b) quantum yield during LP-UV photolysis

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26 (a)

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29 (b)

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32 Fig. S5. Correlation of EEO and UV dose required to achieve 90% removal for TOrCs with
 33 either (a) molar absorption coefficient or (b) quantum yield during MP-UV photolysis

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35 (a)

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38 (b)

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41 Fig. S6. Scores for selection of indicator TORCs in each group to evaluate the performance
42 of (a) LP-UV AOP and (b) MP-UV AOP

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