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Application of surrogates, indicators, and high-resolution mass spectrometry to evaluate the efficacy of UV processes for attenuation of emerging contaminants in water

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Abstract

In response to water scarcity, strategies relying on multiple processes to turn wastewater effluent into potable water are being increasingly considered by many cities. In such context, the occurrence of contaminants as well as their fate during treatment processes is a major concern. Three analytical approaches were used to characterize the efficacy of UV and UV/H₂O₂ processes on a secondary wastewater effluent. The first analytical approach assessed bulk organic parameters or surrogates before and after treatment, while the second analytical approach measured the removal of specific indicator compounds. Sixteen trace organic contaminants were selected due to their relative high concentration and detection frequency over eight monitoring campaigns. While their removal rate ranges from approximately 10 to >90%, some of these compounds can be used to gauge process efficacy (or failure). The third analytical approach assessed the fate of unknown contaminants through high-resolution time-of-flight (TOF) mass spectrometry with advanced data processing and demonstrated the occurrence of several thousand organic compounds in the water. A heat map clearly evidenced compounds as recalcitrant or transformed by the UV processes applied. In addition, those chemicals with similar fate were able to be grouped together into clusters to identify new indicator compounds. In this manuscript, each approach is evaluated with advantages and disadvantages compared.

Keywords

Reuse; Contaminant; Fluorescence; Indicator; Surrogates; Mass Spectrometry; Wastewater; Emerging Contaminants; UV/H₂O₂; HR-TOFMS

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1. Introduction

Water availability has become a major concern over the last decades with resources being threatened by climate change [1–4] and the increasing water demand from growing urban populations [5]. Therefore, in order to sustain their water consumption, several major cities are now considering water reuse strategies such as aquifer recharge with treated wastewater effluent [6].

Wastewater is known to contain a significant amount of trace organic contaminants (TOrcs) such as pharmaceuticals, personal care products, and other constituents or their metabolites [7]. However, conventional wastewater treatment plants generally achieve only limited attenuation of TOrcs, which raises concerns as compounds such as endocrine disruptors have been shown to impact aquatic species at concentrations occurring some municipal wastewater discharges [8]. Therefore, in the context of potable water reuse, the removal of known and unknown TOrcs is not only an important challenge for scientists and engineers but also a major concern for consumers and agencies responsible for protection of public health. Advanced oxidation processes (AOPs) relying on generation of highly reactive hydroxyl radicals are one of the main treatment options applied for water reuse. While several studies have examined the removal of selected TOrcs by UV-based AOPs [9–11], the impact of such treatment on less common TOrcs or unknown compounds is limited. In fact, little is known regarding the complex mixtures of compounds occurring in wastewater and the subsequent transformation products generated by AOPs.

The current research is aimed to compare different analytical approaches for monitoring the efficacy of UV and UV/H₂O₂ processes applied in secondary wastewater effluent. The first analytical approach relied primarily on UV absorbance and fluorescence as a surrogate measurement that could be implemented as online sensors. The second analytical approach relied on liquid chromatography with tandem mass spectrometry (LC-MS/MS) to measure the removal of selected TOrcs referred to as indicators. The third analytical approach relied on liquid chromatography with time-of-flight mass spectrometry (LC-TOF-MS) and advanced data processing capabilities to assess the fate of unknown contaminants including the generation of transformation products. This manuscript provides a critical evaluation of each analytical approach with the aim of guiding researchers and water agencies in the selection of the most suitable technique according to their respective objectives.

2. Materials and Methods

2.1. Wastewater treatment plant and implementation of UV processes

The current study was performed at a 7,500 m³/day capacity wastewater treatment facility located in southern Arizona, USA, receiving mostly domestic wastewater. The raw influent successively went through bar screens, an oxidation ditch for biological nutrient removal, a secondary clarifier, and a sand filter. This secondary wastewater effluent was then partially diverted to a UV and UV/H₂O₂ pilot-scale treatment unit.

The UV-AOP system consisted of a UV reactor (LBX 20) with a single low pressure lamp from Xylem Inc. (Germany) that was capable of treating six m³/h of secondary effluent

(water quality parameters available in supplementary material). Three UV fluences (400, 900 and 1,300 mJ/cm²) typical of AOP applications were applied as calculated from power output of the lamp, UV transmittance, and flow rate of the water. For each UV fluence, three doses of H₂O₂ (0, 1.5 and 3 mg/L) were applied approximately 30 seconds before UV irradiation.

Water samples were collected in amber glass bottles before and after UV-AOP treatment. Within 14 days, several aliquots were taken for analysis by spectrophotometry (UV absorbance and fluorescence) and liquid chromatography with mass spectrometry (LC-MS/MS and LC-TOF-MS).

2.2. UV and fluorescence spectroscopy

UV spectra were acquired using a Varian Cary 50 spectrophotometer with 600 nm/min scan speed at 1 nm resolution and a quartz cell with 10 mm path-length. As for previous studies on water treatment by chlorination [12, 13], UV spectra were overlaid in order to observe isosbestic points which indicate a mass conservation between samples [14].

Sample fluorescence was measured at multiple excitation and emission wavelengths using a Varian Cary Eclipse spectrometer. The excitation wavelength was scanned with a 5 nm resolution over the range 240–450 nm while the emission wavelength was scanned with a 1 nm resolution over the wavelength range of 250–580 nm. For each sample, data were processed using MATLAB software and presented as an excitation-emission matrix (EEM). To remove light scattering, a three-dimensional interpolation method was employed [15]. Inner filter effects (i.e., absorption of excitation and emission light) were corrected using the UV absorbance previously measured according to existing literature [16]. The total fluorescence was then calculated through the regional integration method described in an earlier study [17].

2.3. LC-MS/MS analysis

Considering that more than 65,000,000 chemicals are currently available commercially [18], this present selected limited number of highly-representative indicator TOrCs (Table 1) that were previously reported in wastewater and for which a robust analytical method has available [19]. In this paper, the analytical method was further improved by using online solid-phase extraction [20]. Briefly, aliquots of the samples collected were spiked with stable isotopes of the selected TOrC indicators, then 1.7 mL of sample was loaded onto a PLRP-S 15 µm cartridge using an Agilent 1290 FlexCube. Compounds retained on the cartridge were desorbed directly onto an Agilent Poroshell 120 EC-C18 analytical column (2.1 x 50 mm; 2.7 µm) then separated by liquid chromatography (LC) using an Agilent 1290 series LC system with a gradient of water and acetonitrile, both acidified with 0.1% acetic acid. Once eluted from the column, compounds were detected by tandem mass spectrometry using an Agilent 6460 triple-quadrupole mass spectrometer using the electrospray source with fast polarity switching (simultaneous analysis of positive and negative ions). This method allowed detection limit in the range 0.1–15 ng/L depending on compound properties.

2.4. LC-TOF-MS analysis

The impact of UV-AOP on water composition initially assessed through spectrophotometry and the analysis of selected TOxCs was further examined through comprehensive screening of unknown organic contaminants using an offline solid-phase extraction followed by LC-TOF-MS.

An aliquot (375 mL) of each water sample was loaded on an Oasis Hydrophilic-Lipophilic Balance (200 mg HLB) cartridge from Waters Corporation preconditioned with 5 mL of methanol, 5 mL of methyl tert-butyl ether (MTBE) and 5 mL of reagent water. The cartridge was successively rinsed with 5 mL of reagent water and dried for 30 min with nitrogen. The organic compounds retained on the cartridge were eluted with 5 mL of methanol plus 5 mL of methanol/MTBE (v/v 10/90) then evaporated to 0.5 mL under a gentle flow of nitrogen to achieve a 750x concentration of the initial sample.

Extracts were analyzed in triplicate using a method previously described [21]. Briefly, 3- μ L of extracts were loaded onto an Agilent ZORBAX Eclipse Plus C18 analytical column (2.1 x 50 mm; 1.8 μ m) and separated with a gradient of water and acetonitrile both acidified with 0.1% acetic acid. Detection was accomplished using LC-TOF-MS (Agilent 6540 Q-TOF mass spectrometer) with an electrospray source. In order to detect even unexpected large molecules, mass-to-charge ratios (m/z) in the range 25-3200 were recorded with an acquisition of 2.5 spectra/sec. Advanced data processing was then carried out using the Agilent Mass Profiler Professional Software [21]. However, due to the large amount of data generated, only positive ions were considered in this first attempt of untargeted analysis.

3. Results and Discussion

3.1. Efficacy UV and UV/H₂O₂ processes through surrogates

3.1.1. UV absorbance—The UV spectrum of the secondary wastewater effluent was characterized by a maximum absorbance at 193 nm, a shoulder at 210 nm, and negligible absorbance at wavelengths above 400 nm. After treatment with UV and UV/H₂O₂, the UV absorption spectrum of water samples did not change significantly. In fact, almost no variation in absorbance could be observed when overlaying the spectra. However, zooming on the shoulder of the spectra revealed that the absorbance at 210 nm did not vary with UV treatment alone but increased slightly with the application of UV/H₂O₂. On the contrary, a minor but consistent decrease of the absorbance at 254 nm was observed with the increasing oxidation potential of the treatment applied (Fig. S1), which would be consistent with the transformation of aromatic organic structures. Moreover, two isosbestic points were observed at 231 and 293 nm, which indicate a mass conservation between all samples [14]. The concentrations of water constituents are linked in a way that the mass balance is conserved, as shown in Eq. (1) where C_{ni} is the concentration of the compound n in the sample i and the coefficient a_n does not depend on the sample i .

$$\sum (a_n * C_{ni}) = 1, \forall i \quad (1)$$

Overall, the minor differences among UV spectra tend to indicate a limited impact of UV and UV/H₂O₂ treatment on the secondary wastewater effluent. In addition, the relative amplitude of the UV spectra alteration suggests that increasing the UV fluence has a minor impact compared to the addition of H₂O₂, which is in accordance with the photolysis of peroxide forming hydroxyl radicals known as a strong and non-specific oxidant. Moreover, monitoring UV absorbance also provides some indication on the potential conservation of sample composition and some information on sample chemistry such as the degradation of aromatic compounds. However, low sensitivity is the main limitation of UV spectrophotometry compared to other techniques (Fig. S1) and subtle changes due to water treatment may not be observed.

3.1.2. Fluorescence—The fluorescence profile of the secondary wastewater effluent was characterized by two maxima on the EEM (Fig. 1). The first maximum fluorescence was observed at 340 nm for the excitation and 420 nm for the emission ($\lambda_{\text{ex}} = 340 \text{ nm}$; $\lambda_{\text{em}} = 420 \text{ nm}$) while the second maximum fluorescence was observed at 250 nm for the excitation and 420 nm for the emission ($\lambda_{\text{ex}} = 250 \text{ nm}$; $\lambda_{\text{em}} = 420 \text{ nm}$). Therefore the secondary wastewater effluent mostly contained hydrophobic humic acid-like compounds and hydrophobic fulvic acid-like compounds, according to the multiple EEM regions defined by a previous study [17]. UV treatment alone did not significantly modify the overall fluorescence pattern (Fig. 1), except from a minor but progressive shift of λ_{em} towards lower wavelengths with the increasing UV dose (details in supplementary information, Fig. S2). In oxidation processes, this minor shift is associated with the increase in carbonyl, hydroxyl, alkoxy, amino, and carboxyl groups in the structure of fluorescent dissolved organic matter (DOM). Moreover, the difference in total fluorescence confirmed the decreased concentration of hydrophobic humic acid-like and fulvic acid-like compounds. The addition of H₂O₂ did not significantly modify the fluorescence pattern but dramatically enhanced the impact of UV on the secondary wastewater effluent, as shown by the lower fluorescence intensity depicted by the EEM and the significant reduction of total fluorescence (Fig. 1). Fluorescence spectroscopy through the examination of different EEM regions provides a remarkable representation of the type of DOM in water [17, 22, 23]. Moreover, the comparison of EEMs and the difference in total fluorescence further confirmed that increasing the UV fluence had a minor impact compared to the addition of H₂O₂ within the UV doses applied. Finally, while this was beyond the objectives of the current study, fluorescence could also provide an estimation of by-product formation during water treatment such as the formation of chloroform during chlorination [24].

3.2. Efficacy UV and UV/H₂O₂ processes through indicators

3.2.1. Occurrence of TOrCs in secondary wastewater effluent—The occurrence of TOrCs in the secondary wastewater effluent was characterized before and after UV-AOP. A suite of 29 TOrCs (Table 1) which potentially occur in wastewater and show different vulnerability to UV photolysis and hydroxyl radicals [10, 11, 24–31] were monitored through eight sampling campaigns over 30 months in order to capture potential seasonal variation. The compounds were then arranged into four groups based on their average concentration (Fig. 2). The first group corresponding to compounds quantified above 500 ng/L, and includes TCP, sulfamethoxazole, diclofenac, atenolol, primidone, and

diphenhydramine. The second group which corresponding to compounds in the range of 100–500 ng/L includes: diltiazem, meprobamate, gemfibrozil, carbamazepine, fluoxetine, triclocarban, DEET, benzophenone and trimethoprim. The third group corresponding to compounds in the range 25–100 ng/L includes: triclosan, naproxen, ibuprofen, and caffeine. The fourth group corresponding to compounds quantified below 25 ng/L and includes the 10 remaining chemicals. Finally the monitoring campaigns also resulted in a wide range of detection frequency (14–100%).

The concentration and detection frequency of indicator TOrCs reported in this study are mostly consistent with the type of wastewater received by the treatment facility. While households were the main source of wastewater, it should be noticed that the area is known as a retirement community therefore with a significantly high population of senior citizens. Accordingly, the compounds with the highest concentrations and the highest detection frequencies were mostly pharmaceuticals, including a blood pressure medication and anti-inflammatory medicines often prescribed to an aging population. However, even though the ubiquitous detection of the flame retardant TCPP was anticipated due to its use in domestic products, such a high average concentration was unexpected. Similarly, the constant detection of DEET at relatively high concentration was unexpected for this arid region of Southern Arizona.

The occurrence study also revealed that the 29 TOrCs measured were not all relevant indicators of UV-AOP efficacy. Indeed, a good indicator must combine frequent detection before treatment and sufficient concentration after treatment to ensure the calculation of attenuation. Therefore, the removal of TOrCs was assessed on compounds which had at least 75% detection frequency and 25 ng/L concentration in the secondary wastewater effluent. While fluoxetine was not considered due to the lack of internal standard for its accurate measurement at the time of the UV-AOP experiment, the treatment efficacy evaluation was performed on 16 remaining chemicals.

3.2.2. Attenuation of TOrCs—The restricted list of 16 chemicals showed a wide range of vulnerability to UV-AOP in the conditions tested (Fig. 3). Therefore, these compounds could be grouped according to their removal (low, moderate, high) by both treatment processes and for each dose tested (Table 2). The increasing UV dose alone showed attenuation for some photo-labile compounds, but did not have significant effect on the most recalcitrant chemicals (Fig. 3). For instance, the attenuation of compounds such as diclofenac, triclosan, triclocarban, and sulfamethoxazole which was in the range 38–80% with the lowest UV dose, these could be improved to achieve 68–100% with the highest UV dose. However, increasing the UV dose did not have a significant impact on other chemicals for which attenuation remained below 20%. These results are consistent with previous studies reporting high removals of diclofenac and diltiazem by UV photolysis [11, 32] but poor attenuation of atenolol, ibuprofen, gemfibrozil, carbamazepine, TCPP and DEET [28, 30, 31, 33, 34]. While higher degradation rates of triclosan have been reported in ultrapure water [9], the lower attenuation observed here is consistent with other research showing that a higher DOM concentration tends to reduce efficacy of photolysis of antimicrobial agents in water [35]. In addition, several other studies also reported variability in degradation rates for sulfamethoxazole [34, 36, 37] indicating that, apart from UV dose, water quality

parameters (pH, TOC and concentration of anions) may have a significant impact on the photolysis of some TOrCs [38].

The addition of hydrogen peroxide for advanced oxidation affected differently the removal of the 16 selected TOrCs and particularly increased the process efficacy for those poorly removed by UV alone (Fig. 3). For example, diclofenac and diltiazem which were already well removed by photolysis alone were still attenuated by more than 90% with UV/H₂O₂ while carbamazepine and ibuprofen which were poorly removed by photolysis alone, but have a high hydroxyl radical reaction rate constant (k_{OH} in Table 1), were significantly better attenuated with UV/H₂O₂. However, even with the highest UV and peroxide doses, meprobamate, naproxen, primidone, TCPP and trimethoprim still showed a removal lower than 20%. These results are consistent with the removal of carbamazepine, trimethoprim and primidone by UV/H₂O₂ previously observed in three different wastewaters [39]. Although higher removals were observed for some chemicals in other studies performed in ultrapure water and surface water [34], wastewater has a lower UV transmittance, which reduces the conversion of H₂O₂ into hydroxyl radicals and consequentially decreases the overall efficiency of UV/H₂O₂ processes. Moreover the higher alkalinity and concentration of DOM in wastewater efficiently scavenges hydroxyl radicals, which further reduce the effectiveness of UV/H₂O₂ processes.

The analysis of selected TOrCs by tandem mass spectrometry allowed the accurate calculation of percentage removals. Therefore this approach can be used to determine process failure through a low removal of chemicals vulnerable to UV-AOP such as diclofenac or diltiazem. However, standard tandem mass spectrometry does not provide information regarding the occurrence and fate of unknown TOrCs and, more importantly, does not allow assessing the potential formation of transformation products.

3.3. Efficacy UV and UV/H₂O₂ processes through time of flight mass spectrometry

3.3.1. Occurrence and identification of unknown TOrCs—The large amount of data collected with high-resolution (TOF) mass spectrometry analysis makes the interpretation of total ion chromatograms (TIC) difficult without deconvolution. This operation was performed using the algorithm called “Molecular Feature Extraction” from MassHunter software (Agilent Technologies). Briefly, the algorithm mined the mass spectra acquired across the chromatograms searching for clusters of ions that could represent a compound. For example, a group of two ions or more separated by one m/z typically is representative of a singly charged compound. As a result, the deconvolution isolated 16,778 potential compounds from 18 chromatograms (extract of HPLC grade water used as a blank, extracts of water before treatment, after treatment with three UV doses and after treatment with the highest UV and H₂O₂ doses). This initial data set was then examined using Mass Profiler Professional (MPP) multivariate statistical analysis software (Agilent Technologies). Duplicates due to insignificant retention time shift were discarded and compounds detected in blanks were filtered out. Finally, for improved statistical significance, MPP was set to consider only compounds found in 100% of replicates. After such initial statistical “cleaning” the data set was restricted to 11,804 compounds among which 7,062 occurred in the influent of the UV-AOP pilot (secondary wastewater effluent).

A wide array of TOrCs are expected in wastewater effluent, which should include numerous pharmaceuticals, personal care products, and corresponding metabolites. Many of these substances can be tentatively identified by matching the ion clusters of the high-resolution (TOF) mass spectra with theoretical values from the forensic toxicology (ForTox) database (Agilent Technologies). For example, based on a 94% match of the mass spectrum and in agreement with a previous study [40], the pharmaceutical lamotrigine used to treat epilepsy was identified in the secondary wastewater effluent. Similarly, several hundreds of TOrCs were identified and those with the highest mass spectrum matching score are shown in Table 3. However, despite the very high scores, these preliminary identifications must be considered carefully until further validation is obtained by comparing the retention time and MS/MS pattern with an analytical standard.

Finally, even though it was not in the scope of this article, high resolution (TOF) mass spectrometry also allows identifying transformation products formed during water treatment. For instance, some transformation products previously reported in the literature [41] could also be tentatively identified in this study. However, while transformation products are rarely included in databases, their identification or monitoring is often neglected. Nevertheless, relying on the accurate mass and the isotopic pattern on the mass spectrum, high resolution (TOF) mass spectrometry allows the attribution of a “most probable” chemical formula to each unknown compound that cannot be identified in a library. To obtaining further details on the structure of these unknown compounds would require subsequent analysis of the sample in order to perform high resolution tandem mass spectrometry (QTOF).

3.3.2. Comparison of samples—The data set resulting from the deconvolution and basic statistical “cleaning” described previously was further processed using the MPP software described previously. Initially, a comparison of samples was performed through principal component analysis (PCA). While the PCA plot clearly distinguished samples according to the type of treatment applied, it also showed subtle differences according to the UV dose (Fig. 4). Subsequently, a Venn diagram was used to achieve a more detailed comparison of three specific samples with a first assessment of compound attenuation and byproduct formation (Fig. 4). For instance, while 1,458 compounds were attenuated by both UV (highest dose) and UV/H₂O₂ processes, another 3,421 chemicals appeared resilient. Moreover, 939 byproducts specific to UV and 2,132 others specific to UV/H₂O₂ were formed. Finally, in order to fully visualize the impact of UV-AOP on unknown TOrCs in water, the samples were compared through a heatmap (Fig. 4). On such heatmap the samples are displayed in five columns arranged according to the treatment strength. Each line of each column represents one of the 11,804 compounds of the data set presented earlier. The color scale simulates the concentration of these compounds with blue indicating lower concentration and red higher concentration. The shift in color allows identifying the fate of each contaminant during the treatment. For instance, a compound shifting from red towards blue has a lower concentration after treatment and therefore is attenuated. On the contrary, a compound shifting from blue towards red has a higher concentration after treatment and is a transformation product. Finally those compounds that do not have a strong color shift are recalcitrant to the treatment. By grouping together compounds with similar color shift, the

heatmap quickly reveals clusters of compounds that are attenuated, resilient, or formed (including intermediates). These clusters could be used to identify suitable indicator compounds to represent the larger amount of chemical possible. For instance, using the MPP “find similar entity” feature, it was determined that the compound identified as lamotrigine could serve as an indicator for 1,644 other chemicals including DEET and carbamazepine which had a similar fate during UV-AOP treatment.

High-resolution (TOF) mass spectrometry was shown to provide a sensitive, accurate, and detailed overview of the fate of TOxCs in water during UV-AOP treatment. While this approach implies a complex and time consuming data processing, it can be valuable to select the most suitable indicator compounds that should be monitored by targeted analysis using tandem mass spectrometry. However, high-resolution (TOF) mass spectrometry allows monitoring a large number of TOxCs, but still might represent only a fraction of the total chemical composition of a sample. It should be kept in mind that some compounds might be lost during the sample preparation while others might not ionize in the MS source, suffer from ion suppression, or simply occur at concentrations lower than the detection limit of the instrument.

3.4. Critical comparison of methods for water analysis

The analysis of water samples through multiple approaches performed in the current study shows the consistency of the results provided by different techniques. Recent studies have established a correlation between the measurement of UV absorbance or fluorescence intensity and the removal of TOxCs or formation of disinfection byproducts quantified by mass spectrometry [26, 39, 42]. However, selecting the most suitable analytical technique remains a tradeoff between what the user is expecting from the data (sensitivity and specificity), cost, time, and complexity (Table 4). For instance, when simply trying to detect a change in water composition in order to detect a decreasing performance of a treatment scheme, measuring the UV absorption and/or fluorescence intensity might be the more suitable since it can be performed continuously in real-time and at a lower expense. However, when very high specificity and sensitivity is required, mass spectrometry would become a more appropriate technique. Selecting conventional tandem mass spectrometry or high-resolution (TOF) mass spectrometry will then depend on whether or not the user needs to examine only specific chemicals or if unknown chemicals should also be considered. When selecting high-resolution mass spectrometry, in addition to the cost of analysis, the complexity of the data set and the time required to process it should also be considered. However, even if not necessary at the time of analysis, a researcher may still want to select high-resolution (TOF) mass spectrometry due to a unique advantage of this technique. For instance, the mass spectra acquired can be archived. Therefore, without necessity to reanalyze the sample, the researcher or analyst can still mine the data in the archive even after several years and look specifically for a compound that was not considered when the analysis was originally performed.

4. Conclusion

The impact of UV and UV/H₂O₂ treatment processes on water quality were assessed using several analytical approaches, from the simple measurement of UV absorbance and

fluorescence intensity to the complex analysis of unknown compounds by time-of-flight mass spectrometry. UV irradiation alone with the increasing dose was shown to attenuate some TOrCs in water but the addition of hydrogen peroxide was found to increase significantly the efficiency of the treatment process through the formation of highly reactive radical species.

The different analytical methods employed in this study provided consistent results. Therefore, this paper provides a critical comparison to assist researchers and water treatment utilities in making a decision regarding which technique would be more suitable to monitor water quality according to their own objectives. UV absorbance and fluorescence measurement were shown reliable and relatively inexpensive and could be applied as online sensors at water treatment facilities. Tandem mass spectrometry, on the other hand, constitutes the gold standard technique for a sensitive and accurate measurement of known target compound. When monitoring relevant indicator compounds tandem mass spectrometry can become an effective way to assess the removal of multiple TOrCs during water treatment. High-resolution mass spectrometry; however, can play a major role in order to identify the most appropriate/representative indicator TOrCs and is indispensable to assess the transformation of TOrCs during water treatment. To the best of our knowledge, through the use of high-resolution (TOF) mass spectrometry and advanced data processing tools, this study is the first showing the detection of several thousand compounds in wastewater and providing a clear visualization of their fate during treatment processes. The same approach could also be applied to other treatment processes such as ozonation or chlorination. In the future, the heatmap generated by TOF mass spectrometry should be analyzed in view of toxicity results from bioassays in order to more comprehensively screen water for emerging organic contaminants.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Abbreviations

AOP	Advanced Oxidation Process
DEET	N,N-Diethyl- <i>m</i> -toluamide

LC	Liquid Chromatography
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
PFBS	Perfluorobutanesulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
TCPP	tris(1-chloro-2-propyl) phosphate
TOF	Time of flight TOC, Trace organic contaminant
UV-AOP	UV-based Advanced Oxidation Process

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Highlights

- Two years occurrence data for 29 contaminants in secondary wastewater effluent
- Attenuation of contaminants by UV and UV/H₂O₂ processes
- Identification of compounds with similar behavior during treatment
- First application of sample profiling techniques to assess water quality
- Critical comparison of several analytical approaches for water quality assessment

Figure 1.
Impact of UV and UV/H₂O₂ processes on water composition through fluorescence.

Figure 2.
Occurrence and attenuation of a suite of TORCs in secondary wastewater by UV-AOP.

Figure 3.

Compound identification using high resolution mass spectrometry and databases.

Figure 4. Comparison of water samples exposed to different treatments through advanced processing of high resolution mass spectrometry data.

Table 1

List of selected trace organic contaminants with their properties regarding UV and UV-AOP.

Compound	Class	Susceptibility to UV Photolysis *	$K_{OH} (M^{-1} s^{-1})^{**}$
Atenolol	Pharmaceutical	--	8×10^9
Atrazine	Pesticide	Low	3×10^9
Benzophenone	Personal-care product	--	--
Benzotriazole	Industrial contaminant	--	--
Bisphenol A	Industrial contaminant	--	1×10^{10}
Caffeine	Personal-care product	Low	6×10^9
Carbamazepine	Pharmaceutical	Low	9×10^9
DEET	Personal-care product	Low	5×10^9
Diclofenac	Pharmaceutical	High	8×10^9
Diphenhydramine	Pharmaceutical	Low	5×10^9
Diltiazem	Pharmaceutical	High	--
Estrone	Steroid/Hormone	Moderate	3×10^{10}
Fluoxetine	Pharmaceutical	Low	--
Gemfibrozil	Pharmaceutical	Low	1×10^{10}
Ibuprofen	Pharmaceutical	Low	7×10^9
Meprobamate	Pharmaceutical	Low	4×10^9
Naproxen	Pharmaceutical	Low	1×10^{10}
Norgestrel	Steroid/Hormone	--	--
PFBS	Industrial contaminant	--	--
PFOA	Industrial contaminant	--	--
PFOS	Industrial contaminant	--	--
Primidone	Pharmaceutical	Low	7×10^9
Propylparaben	Personal-care product	--	8×10^9
Simazine	Pesticide	Low	--
Sulfamethoxazole	Pharmaceutical	Moderate	6×10^9
TCPP	Flame retardant	Low	3×10^8
Triclocarban	Personal-care product	Moderate	1×10^{10}
Triclosan	Personal-care product	Moderate	1×10^{10}
Trimethoprim	Pharmaceutical	Low	7×10^9

* According to existing literature [11, 24, 28, 30]

** According to existing literature [10, 25–27, 29, 31]

Attenuation of selected trace organic contaminants by UV and UV/H₂O₂

Table 2

	Low UV dose (≤ 500 mJ/cm ²)				Medium UV dose (500–1000 mJ/cm ²)				High UV dose (> 1000 mJ/cm ²)			
	Low removal (0–30%)		Moderate removal (30–70%)		Low removal (0–30%)		Moderate removal (30–70%)		Low removal (0–30%)		Moderate removal (30–70%)	
	High removal (70–100%)	Diltiazem	Diltiazem	Diltiazem	High removal (70–100%)	Diltiazem	Diltiazem	Diltiazem	High removal (70–100%)	Diltiazem	Diltiazem	Diltiazem
H ₂ O ₂ Dose 0 mg/L	Atenolol	Sulfamethoxazole	Triclosan	Triclosan	Atenolol	Trimehoprim	Trimehoprim	Trimehoprim	Atenolol	Trimehoprim	Diphenhydramine	Diltiazem
	Trimehoprim	Triclosan	Triclosan	Triclosan	Trimehoprim	Trimehoprim	Trimehoprim	Trimehoprim	Trimehoprim	Trimehoprim	Diphenhydramine	Diltiazem
	Primidone	Triclosan	Triclosan	Triclosan	Primidone	Trimehoprim	Trimehoprim	Trimehoprim	Primidone	Trimehoprim	Diphenhydramine	Diltiazem
	Meprobamate	Triclosan	Triclosan	Triclosan	Meprobamate	Trimehoprim	Trimehoprim	Trimehoprim	Meprobamate	Trimehoprim	Diphenhydramine	Diltiazem
	Diphenhydramine	Triclosan	Triclosan	Triclosan	Diphenhydramine	Trimehoprim	Trimehoprim	Trimehoprim	Carbamazepine	Trimehoprim	Diphenhydramine	Diltiazem
	Carbamazepine	Triclosan	Triclosan	Triclosan	Carbamazepine	Trimehoprim	Trimehoprim	Trimehoprim	DEET	Trimehoprim	Diphenhydramine	Diltiazem
	DEET	Triclosan	Triclosan	Triclosan	DEET	Trimehoprim	Trimehoprim	Trimehoprim	Naproxen	Trimehoprim	Diphenhydramine	Diltiazem
	Naproxen	Triclosan	Triclosan	Triclosan	Naproxen	Trimehoprim	Trimehoprim	Trimehoprim	TCPP	Trimehoprim	Diphenhydramine	Diltiazem
	TCPP	Triclosan	Triclosan	Triclosan	TCPP	Trimehoprim	Trimehoprim	Trimehoprim	Ibuprofen	Trimehoprim	Diphenhydramine	Diltiazem
	Ibuprofen	Triclosan	Triclosan	Triclosan	Ibuprofen	Trimehoprim	Trimehoprim	Trimehoprim	Genfibrozil	Trimehoprim	Diphenhydramine	Diltiazem
	Genfibrozil	Triclosan	Triclosan	Triclosan	Genfibrozil	Trimehoprim	Trimehoprim	Trimehoprim				
H ₂ O ₂ Dose 3 mg/L	Atenolol	Sulfamethoxazole	Triclosan	Triclosan	Atenolol	Trimehoprim	Trimehoprim	Trimehoprim	Atenolol	Trimehoprim	Diphenhydramine	Diltiazem
	Trimehoprim	Triclosan	Triclosan	Triclosan	Trimehoprim	Trimehoprim	Trimehoprim	Trimehoprim	Trimehoprim	Trimehoprim	Diphenhydramine	Diltiazem
	Primidone	Triclosan	Triclosan	Triclosan	Primidone	Trimehoprim	Trimehoprim	Trimehoprim	Primidone	Trimehoprim	Diphenhydramine	Diltiazem
	Meprobamate	Triclosan	Triclosan	Triclosan	Meprobamate	Trimehoprim	Trimehoprim	Trimehoprim	Meprobamate	Trimehoprim	Diphenhydramine	Diltiazem
	Diphenhydramine	Triclosan	Triclosan	Triclosan	Diphenhydramine	Trimehoprim	Trimehoprim	Trimehoprim	Naproxen	Trimehoprim	Diphenhydramine	Diltiazem
	Carbamazepine	Triclosan	Triclosan	Triclosan	Carbamazepine	Trimehoprim	Trimehoprim	Trimehoprim	TCPP	Trimehoprim	Diphenhydramine	Diltiazem
	DEET	Triclosan	Triclosan	Triclosan	DEET	Trimehoprim	Trimehoprim	Trimehoprim	Genfibrozil	Trimehoprim	Diphenhydramine	Diltiazem
	Naproxen	Triclosan	Triclosan	Triclosan	Naproxen	Trimehoprim	Trimehoprim	Trimehoprim				
	TCPP	Triclosan	Triclosan	Triclosan	TCPP	Trimehoprim	Trimehoprim	Trimehoprim				
	Ibuprofen	Triclosan	Triclosan	Triclosan	Ibuprofen	Trimehoprim	Trimehoprim	Trimehoprim				
	Genfibrozil	Triclosan	Triclosan	Triclosan	Genfibrozil	Trimehoprim	Trimehoprim	Trimehoprim				

Table 3

Tentative identification of some TOxCs in pilot influent using high resolution mass spectrometry and the ForTox compound database

Compound	Formulae	Score	Compound	Formulae	Score
4-EMC /4-Ethylmethcathinone	C12 H17 N O	99.81	Meloxicam	C14 H13 N3 O4 S2	98.28
Trioxysalen	C14 H12 O3	99.74	7-Acetaminonitrazepam	C17 H15 N3 O2	98.25
Azoxystrobin	C22 H17 N3 O5	99.72	Diuron	C9 H10 Cl2 N2 O	98.2
Oxisuran	C8 H9 N O2 S	99.72	Morclofone	C21 H24 Cl N O5	98.19
2-Methylamino-5-chlorobenzophenone (Diazepam HY)	C14 H12 Cl N O	99.7	Cortolone	C21 H34 O5	98.17
Caprylic acid octanoic acid	C8 H16 O2	99.66	Kresoxim-methyl	C18 H19 N O4	98.15
Propafenone	C21 H27 N O3	99.6	Telmisartan	C33 H30 N4 O2	98.04
Falipamil	C24 H32 N2 O5	99.57	Homosalate	C16 H22 O3	97.86
Dimantine (Dymanthine)	C20 H43 N	99.56	Arachidonic acid	C20 H32 O2	97.83
Gabapentin	C9 H17 N O2	99.54	Cetirizine	C21 H25 Cl N2 O3	97.81
Lopinavir	C37 H48 N4 O5	99.54	Benzisoxazole acetamidoxime	C9 H9 N3 O2	97.72
Mazindol	C16 H13 Cl N2 O	99.42	Phenisonone	C12 H17 N O3	97.58
Imidocarb	C19 H20 N6 O	99.22	Doxazosin	C23 H25 N5 O5	97.53
Carbamazepine	C15 H12 N2 O	99.12	Picrotoxinin	C15 H16 O6	97.41
Dimetofrine	C11 H17 N O4	99.12	Promoxolane	C10 H20 O3	97.34
Diclofenac	C14 H11 Cl2 N O2	99.08	Trimetazidine	C14 H22 N2 O3	97.29
Fenetradil	C22 H36 N2 O3	99.06	Nesapidil	C23 H28 N4 O4	97.08
Boscalid (Nicobifen)	C18 H12 Cl2 N2 O	99.01	Acetylcysteine	C5 H9 N O3 S	97.07
Omoprostil	C23 H38 O6	99.01	Triclocarban	C13 H9 Cl3 N2 O	97.06
Cyprofuram	C14 H14 Cl N O3	98.99	Propiram	C16 H25 N3 O	97.03
Diphenamid	C16 H17 N O	98.92	4-Hydroxypyrrolidyltryptamine	C14 H18 N2 O	97.02
O-1821	C17 H22 O2	98.85	Triazamate	C13 H22 N4 O3 S	97
Celecoxib	C17 H14 F3 N3 O2 S	98.81	Undecenamide 10-	C11 H21 N O	96.99
Ketocainol	C18 H31 N O2	98.81	Valsartan	C24 H29 N5 O3	96.98
Bezitramide	C31 H32 N4 O2	98.8	β-D	C11 H15 D2 N O3	96.98
Tolnidamine	C16 H13 Cl N2 O2	98.79	Fluoxetine	C17 H18 F3 N O	96.75
Ethinylcyclohexanol	C8 H12 O	98.76	Riluzole	C8 H5 F3 N2 O S	96.74
Norcodeine	C17 H19 N O3	98.76	Cloxacillin	C19 H18 Cl N3 O5 S	96.68

Compound	Formulae	Score	Compound	Formulae	Score
Trimecain	C15 H24 N2 O	98.76	4'-Hydroxynordiazepam	C15 H11 Cl N2 O2	96.51
Loxoprofen	C15 H18 O3	98.67	Diacetylaminoazotoluol	C18 H19 N3 O2	96.49
Anisotropine	C16 H29 N O2	98.56	Methadone	C21 H27 N O	96.4
Benzenesulfonamide	C6 H7 N O2 S	98.56	Flufenprox	C24 H22 Cl F3 O3	96.37
19-Norandrostenedione	C18 H24 O2	98.53	Dyclonine	C18 H27 N O2	96.35
Denopamine	C18 H23 N O4	98.53	Warfarin	C19 H16 O4	96.33
Isosteviol	C20 H30 O3	98.51	Oxacillin	C19 H19 N3 O5 S	96.3
Pyridinolcarbamate	C11 H15 N3 O4	98.5	Acridine (Carbamazepine-M)	C13 H9 N	96.23
Nordiazepam	C15 H11 Cl N2 O	98.46	Gemcitabine	C9 H11 F2 N3 O4	96.16
Clopidogrel	C16 H16 Cl N O2 S	98.44	Metaldelhyde	C8 H16 O4	96.09
Losindol	C19 H20 Cl N	98.4	Paliperidone (9-Hydroxyrisperidone)	C23 H27 F N4 O3	96.09
Oletimol	C15 H15 N O	98.39	Mecinarone	C24 H27 N O6	95.96

Table 4

Critical comparison of analytical methods for the assessment of water quality

Criteria	Sub-criteria	UV absorption	Fluorescence	Conventional	Tandem Mass Spectrometry	High Resolution Mass Spectrometry
Cost	Instrumentation	Low	Low	High		Very High
	Personnel (qualification)	Low	Low	High		High
	Logistics (maintenance, space...)	Low	Low	High		High
Time	Sample Preparation	Minutes	Minutes	Minutes-Hours		Minutes-Hours
	Analysis	Seconds-Minutes	Minutes	Minutes		Minutes
	Data Processing	Minutes	Minutes-Hours	Hours		Hours-Days
Complexity	Instrument Use	Low	Low	High		Very High
	Data Interpretation	Low	Low	Moderate		High
Data Acquisition	Amount of Data	Low	Low	Moderate		Very High
	Specificity	Very Low	Low	Very High		Very High
	Sensitivity	Very Low	Moderate	Very High		High