

Transformation products of contaminants of emerging concern in water by UV-based processes

Danilo Bertagna Silva ^{a,*}, Gianluigi Buttiglieri^{b,c}, Maria José Farré^{b,c} and Sandra Babić^a

^a Faculty of Chemical Engineering and Technology, University of Zagreb, Trg Marka Marulića 19, 10000 Zagreb, Croatia

^b Catalan Institute for Water Research (ICRA-CERCA), C. Emili Grahit 101, 17003 Girona, Spain

^c University of Girona, Girona, Spain

*Corresponding author. E-mail: dsilva@fkit.hr

 DBS, 0000-0003-4413-7108

ABSTRACT

Contaminants of emerging concern (CECs) and their respective transformation products (TPs) formed following photodegradation pose considerable threats to the environment and our health. The formation of TPs during UV-LED-based degradation of three target pollutants in the EU Watch List of CECs was accessed by LC-MS-Orbitrap, and their reaction pathways were elucidated. The influence of different matrices and treatments of choice on TP formation was investigated. Results showed that matrix changes did not produce different reaction pathways during UV-A photocatalysis, although plots of TP peak areas vs. time were different for each case. A new TP was found for the antidepressant venlafaxine, (1-[2-(dimethylnitroxy)-1-(4-methoxyphenyl)ethyl]cyclohexanol. When comparing UV-A photocatalysis with UV-C photolysis, dissimilar pathways were observed due to the distinct reaction mechanisms of each process, since photocatalysis, unlike photolysis, relies on radical-based reaction routes. Different levels of confidence were obtained for each TP depending on the availability of MS² data in the literature and of standards for comparison. All the found TPs had similar molecular masses in comparison to their respective parent compounds. Most of the TPs remained in the effluent after 6 hours of photodegradation, which highlights the importance of their control, close-monitoring, and further toxicity assessments.

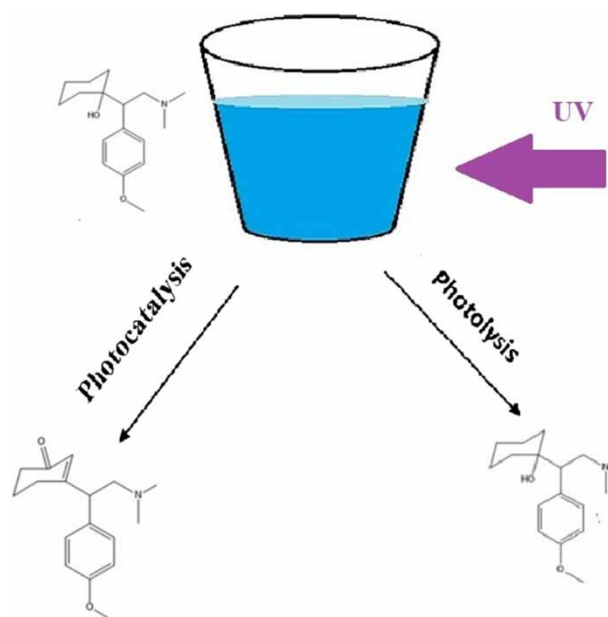
Key words: Orbitrap, photodegradation, transformation products, trimethoprim, venlafaxine

HIGHLIGHTS

- Detection of transformation products of contaminants of emerging concern in water.
- Elucidation of reaction pathways for photolysis and photocatalysis.
- A new transformation product found for venlafaxine.
- No difference in detected compounds for tap and ultrapure water.

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GRAPHICAL ABSTRACT



1. INTRODUCTION

Reports confirming the presence of contaminants of emerging concern (CECs) in water bodies in ranges varying from nanograms to micrograms per litre have been ubiquitous in literature (Corrêa *et al.* 2021; Llamas-Dios *et al.* 2021; Malnes *et al.* 2022; Wilkinson *et al.* 2022). Even in these small amounts, many studies showed that these substances can cause harm to aquatic organisms and people (Shao *et al.* 2019; Kasonga *et al.* 2021; Podder *et al.* 2021; Saidulu *et al.* 2021). Although the synergistic toxic effect of hundreds (or thousands) of these substances is highly unpredictable (Yashas & Sadashiva Murthy 2017), the most frequently raised concerns are regarding alterations in the reproductive cycle of fish (Jacquin *et al.* 2020), hormonal dysfunctions (Acir & Guenther 2018; Kasonga *et al.* 2021; Saidulu *et al.* 2021), and cancer (Paumgartten 2020; Kasonga *et al.* 2021). Since most of these compounds come from anthropogenic sources (Bertagna Silva *et al.* 2020) (e.g., pesticides, pharmaceuticals, cosmetics, flame retardants), they generally have slow biodegradation routes and tend to persist and bioaccumulate in the environment; biomagnifying in trophic levels of food chains (Zhang *et al.* 2019; Menéndez-Pedriza & Jaumot 2020). Because of that, conventional wastewater treatment plants are not capable of removing all these compounds satisfactorily and end up being hotspots sinks for CECs (Miklos *et al.* 2018a, 2018b; Teodosiu *et al.* 2018).

Transformation products (TPs) are an umbrella term to define compounds that are formed by subsequent reactions of the parent compound. These reactions may take place inside living organisms (e.g., biodegradation, formation of metabolites) (Wilkinson *et al.* 2017) and in the environment (e.g., solar photolysis and hydrolysis) (Trovó *et al.* 2009). TPs can also be formed in a more controlled environment, during water or wastewater treatment processes (Yin *et al.* 2017). TPs can be the result of any reaction which does not completely mineralize the target pollutant to water and carbon dioxide. The persistence of most CECs allows parent compounds and their TPs to have long half-lives in the environment, moving from water to soil; from fat tissues to air and vice versa (Periša *et al.* 2013; Luo *et al.* 2014). A study found, for example, that the concentration of the metabolite *o*-desmethylvenlafaxine was higher than its respective parent compound, venlafaxine, in wastewater treatment plants (Lajeunesse *et al.* 2012). TPs can cause, in some cases, more harm to living organisms than their respective parent compounds, so attention must be paid to the risk of their generation (Silva *et al.* 2016). Many reports have shown, in fact, an increase in the toxicity after chemical oxidation treatment due to the formation of highly toxic TPs (Silva *et al.* 2016; Alharbi *et al.* 2017; Sharma *et al.* 2018; Rueda-Marquez *et al.* 2020).

The awareness of the threat posed by CECs and their TPs was only possible due to the recent development and optimization of analytical techniques which allowed the detection and quantification of these substances in the environment (Pérez-Lemus *et al.* 2019; Beccaria & Cabooter 2020). Liquid chromatography–high-resolution

mass spectrometry (LC-HRMS) methods provide different modes of acquisition, such as the full-scan and the selected-ion mode. The latter is particularly useful for quantitative analysis of TPs which are already expected during degradation. The mode selection is related to the choice of screening procedure for determination of molecules, relying on the availability of a known standard. In case the standard is available, target screening is made via direct comparison of spectra. If standards are not available, but are predictable, suspect screening on an exact mass range is done and structure can be confirmed with MS databases and other prediction tools. In case the sample is completely unknown, non-target analysis gives the most prominent peaks and allows an attempt of TP identification (Picó & Barceló 2015; Grund *et al.* 2016; He & Aga 2019; Paíga *et al.* 2019). More often than not, TP analysis is carried out by suspect screening (Badea *et al.* 2020).

Photodegradation-based processes using ultraviolet (UV) radiation such as photolysis and photocatalysis are capable of degrading CECs by different reaction routes (Zaveri *et al.* 2018; Bertagna Silva *et al.* 2022). Photolysis and photocatalysis are two different processes which rely on different mechanisms. While photolysis consists of the direct breaking of molecular bonds via high-energy photons, photocatalysis depends on the presence of a photoactive catalyst (e.g., TiO₂) that, when properly illuminated, will generate highly reactive unstable species (such as the hydroxyl and the superoxide radical) on its surface, further oxidizing the target pollutant in the effluent (Bertagna Silva *et al.* 2022). Photolysis is widely used in water treatment plants since it allows pathogen control via disinfection (Trovó *et al.* 2009), while photocatalysis has a fast-growing interest by the academia and society due to its potential to degrade CECs, albeit facing hurdles regarding its energetic and economic performance (Bertagna Silva *et al.* 2020).

The influence of matrix composition in these processes has been widely discussed, being one of the main aspects to consider when optimizing CEC degradation performance (García-Galán *et al.* 2016; Miklos *et al.* 2018a, 2018b; Bertagna Silva *et al.* 2020). The influence of pH, the presence of natural organic matter (NOM), and inorganic salts can either improve or hinder degradation performance by scavenging radical oxygen species (ROS), photosensitization, and/or light screening effect (Martínez-Costa *et al.* 2018; Bertagna Silva *et al.* 2022).

The objective of this research was to investigate how different are the TPs of three pharmaceuticals, currently at the EU Watch List of Contaminants of Emerging Concern (European Commission 2020), under different reaction scenarios and identified by high-resolution LC-MS-Orbitrap. The chosen pharmaceuticals were the antibiotic trimethoprim (TMP), the antidepressants venlafaxine (VEN), and *o*-desmethylvenlafaxine (DV). Previous studies were able to detect TPs from the photodegradation of the target compounds using different MS methods (García-Galán *et al.* 2016; Lambropoulou *et al.* 2017; Cai & Hu 2018). The formation of TPs can increase the toxicity of the effluent and the compounds which have been routinely signalled as precursors of highly toxic TPs should be properly identified, monitored, and handled. Possible TPs and their degradation pathways were proposed for UV-A photocatalysis performed in Milli-Q[®] (MQ) water and in tap water. Comparisons were also made between the TPs formed by UV-A photocatalysis and UV-C photolysis for experiments performed in MQ water, to investigate how these processes may lead to the formation of different TPs.

2. MATERIALS AND METHODS

2.1. Chemicals and reagents

High purity (>98%) analytical standard of TMP (CAS no. 738-70-5) was supplied from Sigma-Aldrich (St. Louis, USA). VX (CAS 99300-78-4) and DV (CAS no. 93413-62-8) were supplied by Tokyo Chemical Industry Co. Ltd (Tokyo, Japan). HPLC grade methanol (CAS no. 67-56-1) was supplied by Fisher Scientific Ltd (UK).

2.2. Water matrices

The UV-A photocatalytic degradation of pharmaceuticals was investigated in two water matrices: ultrapure water (MQ) and tap water. Photolysis was performed using UV-C in MQ water only. UV-A photolysis was not performed since previous research showed that the three target pollutants are not degraded by it (Bertagna Silva *et al.* 2022). Also based on this previous work, UV-C photocatalysis was not performed due to its poor performance caused by the high absorptivity of the UV-C rays on the catalyst, reducing the system's photonic efficiency. MQ water was prepared by the Millipore Simplicity UV-system (Millipore Corporation, Billerica, USA). Tap water was sampled at the laboratory faucet at the Catalan Institute for Water Research (ICRA, Girona, Spain). Prior to the sampling, the faucet was turned on and left to run at a uniform rate to flush standing water from

the service pipes (2–3 min). Tap water was analysed for pH, total organic carbon (TOC), and inorganic ion content. Supplementary Table S1 shows the composition of tap water.

2.3. Experimental set-up and degradation tests

The experimental set-up of the UV-LED photoreactor is used in previous works (Bertagna Silva *et al.* 2021, 2022). Briefly, two identical cylindrical quartz reaction vessels with an inner diameter of 37 mm, length = 150 mm, and wall thickness = 1.5 mm were adopted (total volume of 150 mL). In one of them, nanostructured TiO₂ film was immobilized on its inner sidewall by a sol-gel method and a dip-coating technique. The preparation of nanofilm, its characterization, and immobilization are described in detail by Čizmić *et al.* (2019). A schematic drawing of the experimental set-up can be found in Bertagna Silva *et al.* (2021). Six UV-LED strips, altering between UV-C and UV-A light, were attached to the support as external vertical columns. The light sources were all facing towards the cylinder's central axis and their distribution was radially symmetric, with intervals of 60°. Using the control board, it was possible to choose which wavelength would be used (either UV-A or UV-C).

UV-LED strips in the UV-A range (365 nm) and UV-C range (272 nm) were provided by Waveform Lighting (Vancouver, USA). Photometric specifications, emission spectrum, dimensions, and other data are available in the product's specification datasheet and can also be found in previous works (Waveform Lighting 2020a, 2020b; Bertagna Silva *et al.* 2022). All experiments were performed in a dark room, with constant stirring by a magnetic bar. The temperature of the reaction solution remained at (21.0 ± 2.0)°C throughout the experiments by the addition of a table fan.

Initial solutions containing 10 mg/L of each target pollutant, individually, were prepared in MQ and tap water. Higher concentrations than the ones usually found in realistic environmental conditions were adopted to facilitate TP elucidation. Reaction time for all experiments was 6 h. Samples were collected at fixed intervals for further analysis.

2.4. Analytical determination

Samples were directly analysed by LC-MS-Orbitrap (Orbitrap Exploris 120, Thermo Fisher Scientific, Massachusetts, USA). The instrument consists of a quadrupole-orbitrap analyser with a Q-trap for high-resolution accurate mass capability. The ion source is heated-electrospray ionization. The separation was carried out on the Hypersil gold column (50 mm × 2 mm, particle size 1.9 µm, Thermo Scientific). The software Compound Discoverer 3.3 (Thermo Fisher, MA, USA) was used for data analysis. Prior to it, samples were diluted 50-fold in MQ water and filtered through a PVDF syringe filter 0.22 µm.

A gradient chromatographic method using MQ water (A) in methanol (B) was developed. Initially, the volume proportion of A:B was 98:2 until $t = 4.75$ min, when a linear gradient elution was applied. The proportion 2:98 was obtained at $t = 6$ min and kept constant until $t = 9$ min. At this point, the composition had a step change back to the initial one (2% B) until the end of elution ($t = 12$ min).

The Compound Discovery Software was used in both full-scan mode with an m/z range from 100 to 1,000 and selected-ion monitoring in the positive polarity. The Orbitrap resolution was 6,000 for MS and 15,000 for MS². A literature review on the topic was made to list the most common previously obtained TPs for all the target pollutants in both photolytic and photocatalytic routes (Sirtori *et al.* 2010; García-Galán *et al.* 2016; Alharbi *et al.* 2017; Giannakis *et al.* 2017; Martínez-Costa *et al.* 2018; Osawa *et al.* 2019). According to the scheme of communicating confidence of small molecules proposed by Schymanski *et al.* (2014), the structures of possible TPs were suggested. If a TP matches an available standard, it is given the level 1 of confidence, 'confirmed structure'. If the software was able to identify a compound based on its database in full-scan mode (comparing MS² data), the TP was considered a 'probable structure'. If the software could not find any correspondent structure in its MS² database, the TP was considered a 'tentative candidate' if its molecular formula and MS² spectra matches with previously detected compounds found in previous studies performed under similar reaction conditions.

3. RESULTS AND DISCUSSION

3.1. UV-A photocatalysis: MQ and tap water

Figure 1 shows degradation plots vs. time for each of the three target pollutants for individual UV-A photocatalysis experiments performed in MQ water and tap water, respectively. Analysing Figure 1(a), TMP was the only compound that was completely degraded after 6 h of reaction, while VEN and DV reached 53 and 73% of degradation, respectively. On the other hand, Figure 1(b) shows how tap water affected degradation of each

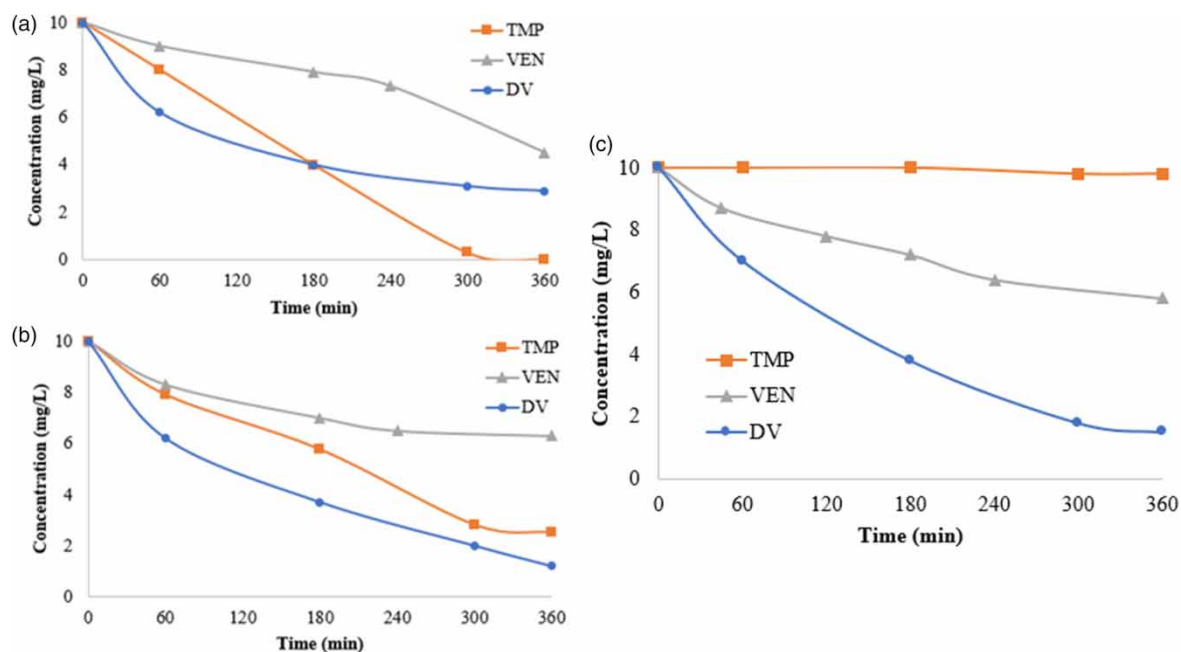


Figure 1 | Degradation plots by UV-A photocatalysis of the target pollutants in MQ water (a) and tap water (b) and UV-C photolysis in MQ water (c).

pharmaceutical uniquely. TMP reacted slower than in MQ water, reaching only 78% of degradation after 6 h. VEN similarly reached 40% of degradation after 4 h and remained stable until the end of the experiment. By contrast, reactivity of DV was enhanced in tap water, reaching 90% of degradation after 6 h.

Direct comparison of degradation performance with previous literature is difficult, since reaction parameters such as photoreactor geometry, pollutant initial concentration, light intensity, catalyst form (slurry vs. immobilized), composition, and surface area all vary considerably (Cai & Hu 2017; Lambropoulou *et al.* 2017; Miklos *et al.* 2018a, 2018b). Data of degradation of these substances in real matrices is also scarce (Giannakis *et al.* 2017; Bertagna Silva *et al.* 2020; Mpatani *et al.* 2021). Tap water's composition also varies considerably across the world, containing multiple substances which may affect photocatalytic degradation rates of CECs, either positively or negatively depending on each scenario. Typically, inorganic salts (e.g., carbonates and bicarbonates) and NOM present in tap water act as radical scavengers, hindering degradation of the target compounds (García-Fernández *et al.* 2015; Silva *et al.* 2018; Bertagna Silva *et al.* 2022). However, the pH of tap water is also significantly important for the determination of adsorption rates of target pollutants on the catalyst's surface and for the overall production of radicals. Tap water of higher pH may increase the formation of hydroxyl radical (García-Fernández *et al.* 2015). The system's pH will depend not only on the initial matrix composition, but also on (a) the initial concentration of the target pollutant and its respective pK_a value; (b) the formation of multiple TPs and their possible reactions with other substances in the matrix. Because of that, the photocatalytic response of each target pollutant can differ considerably as a function of the matrix and its modifications, as well as the reactivity of the target compound with each different ROS formed during photocatalysis (Bertagna Silva *et al.* 2022). As observed in this study, tap water can either increase or reduce pollutant's photocatalytic degradation depending on how each target molecule will respond to this multitude of factors affecting it simultaneously.

Table 1 shows the TPs identified in all the performed UV-A photocatalysis experiments. The same TPs were observed in both MQ and tap water. In terms of identification confidence, most of the TPs were of probable structure or tentative candidate, due to the lack of availability of standards for confirmation. The only exception was DV, which was one of the TPs obtained from the degradation of VEN (beyond being a pharmaceutical by itself) and it could be directly compared with the corresponding standard. MS² spectra for all the identified substances are shown in Supplementary Figures S1–S5.

Although the same TPs were observed in both matrices, the intensity of the peaks was different. Supplementary Figures S6 and S7 show the monitoring of TP integration peaks along the reaction time for the three target

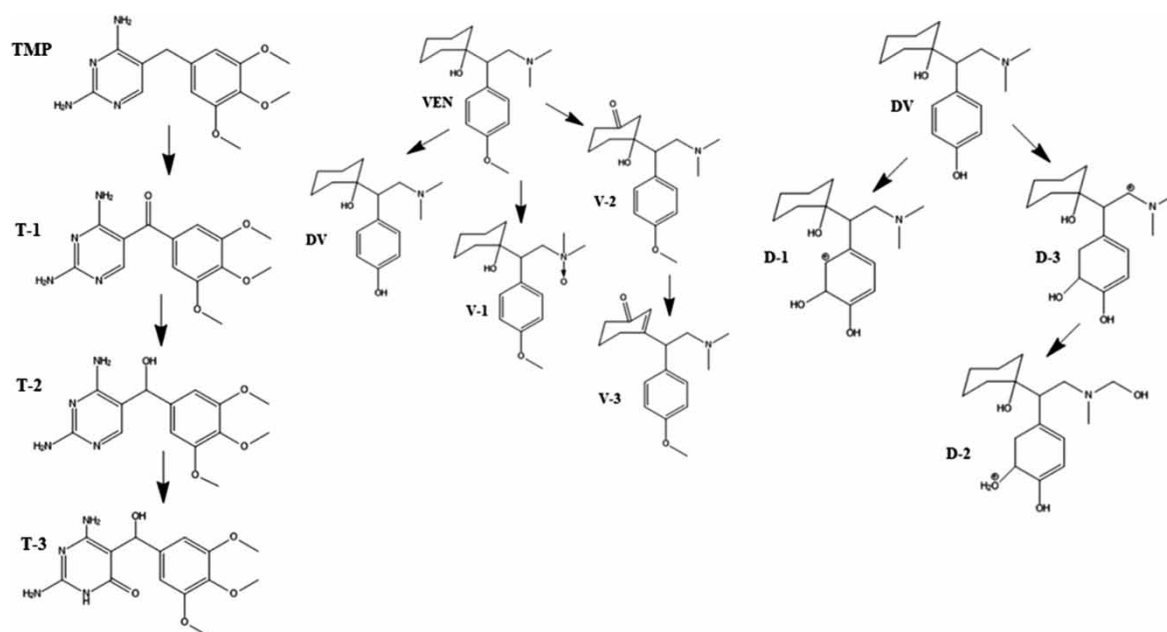
Table 1 | TPs formed by UV-A photocatalysis in both MQ and tap water

TP	Parent compound	m/z (M + H ⁺)	RT (min)	Chemical formulae	Mass error (ppm)	Reaction	Identification confidence	Ref.
T-1	TMP	305.104	2.095	C ₁₄ H ₁₆ N ₄ O ₄	-1.23	O	Probable structure	Samy <i>et al.</i> (2020) and Sirtori <i>et al.</i> (2010)
T-2	TMP	307.139	1.584	C ₁₄ H ₁₈ N ₄ O ₄	-1.35	H	Probable Structure	Alharbi <i>et al.</i> (2017) and Sirtori <i>et al.</i> (2010)
T-3	TMP	323.134	1.781	C ₁₅ H ₁₈ N ₄ O ₅	-1.34	H, O	Tentative candidate	Yang <i>et al.</i> (2020)
DV	VEN	264.195	2.091	C ₁₆ H ₂₅ NO ₂	-1.25	DM	Confirmed structure	Giannakis <i>et al.</i> (2017) and Lambropoulou <i>et al.</i> (2017)
V-1	VEN	294.206	2.242	C ₁₇ H ₂₇ NO ₃	-1.27	O	Probable structure	New
V-2	VEN	292.190	1.617	C ₁₇ H ₂₅ NO ₃	-1.10	DS, O	Tentative candidate	Giannakis <i>et al.</i> (2017) and Osawa <i>et al.</i> (2019)
V-3	VEN	274.179	2.141	C ₁₇ H ₂₃ NO ₂	-0.87	DH	Tentative candidate	Martínez-Costa <i>et al.</i> (2018)
D-1	DV	280.190	1.434	C ₁₆ H ₂₅ NO ₃	-1.22	O	Tentative candidate	García-Galán <i>et al.</i> (2016)
D-2	DV	296.185	1.147	C ₁₆ H ₂₅ NO ₄	-1.47	O	Tentative candidate	García-Galán <i>et al.</i> (2016)
D-3	DV	278.174	1.940	C ₁₆ H ₂₃ NO ₃	-1.59	DS, O	Tentative candidate	García-Galán <i>et al.</i> (2016)

RT, retention time; O, oxidation; H, hydroxylation; DM, demethylation; DS, desaturation; DH, dehydration.

pollutants in MQ and tap water matrices, respectively. The same signal intensity can correspond in reality to different concentrations. Care should thus be taken to this type of studies, since the presence of new TPs could be underestimated or overestimated, based only in the relative areas. Accurate quantification and further evaluation of the results can only be performed using the corresponding standards (Rubirola *et al.* 2014). By comparing both cases, it can be seen that T-1 of TMP was the most prevalent TP throughout the whole degradation process in tap water. All TPs formed during VEN and DV degradation had smaller peaks in tap water than in MQ.

Figure 2 shows the proposed degradation pathways and TPs formation of the three target compounds by means of UV-A photocatalysis. Analysing the TPs of TMP, T-1 and T-2 were formed by the oxidation of the bridging

**Figure 2** | Proposed formation of TPs by UV-A photocatalysis.

methyl group between the two rings. Similar results were obtained elsewhere (Zwiener 2007; Sirtori *et al.* 2010; Martínez-Costa *et al.* 2018). T-3 was detected by the Orbitrap (smaller peak areas compared to T-1 and T-2) and it can be related to the oxidation of the pyrimidine 2,4-diamine ring (Yang *et al.* 2020). After 5 h of experiment, all the formed T-3 had been consumed. Regardless of the parent compound being completely removed after 6 h of treatment, TPs of TMP other than these three could not be found.

The TP of VEN with the highest peak area was DV and it was the only one that could be confirmed by direct MS² comparison with the corresponding standard. DV is formed by demethylation of VEN. The other TPs are related to oxidation at different points of the molecule (Lambropoulou *et al.* 2017). It should be highlighted that the compound V-1 (1-[2-(dimethylnitrolyl)-1-(4-methoxyphenyl)ethyl]cyclohexanol), identified by the software as a probable structure (MS² compared to database) had not been previously mentioned in the literature as a degradation product of VEN. Demethylation, however, was not observed for TMP. A hypothesis is that the bridging methyl group in this molecule acts as a more attractive reaction point. As for DV, the degradation pathways followed the hydroxylation of the aromatic ring, as previously described in Samy *et al.* (2020).

3.2. UV-A photocatalysis and UV-C photolysis in MQ water

As explained in the introduction, photocatalysis and photolysis rely on different reaction mechanisms (Guo *et al.* 2013; Hu *et al.* 2020; Bertagna Silva *et al.* 2020); therefore, the degradation of the same target pollutant can result in different TPs depending on the method of choice. Previous studies have suggested that photocatalysis is more efficient for CEC degradation in the presence of UV-A than UV-C, since the latter is more prone to suffer *screening effects* by the catalyst due to UV-C's higher absorptivity in comparison to UV-A (Bertagna Silva *et al.* 2022). This one, in its turn, is not as capable of causing photolytic reactions due to its lower energy character, in comparison to UV-C (Mason *et al.* 2016; Bertagna Silva *et al.* 2022). Comparing these two different processes contributes to elucidate their different TPs and results in a better understanding of their degradation routes.

Figure 1(c) shows the degradation of the three target pollutants by UV-C photolysis in MQ water. TMP reactivity to UV-C photolysis was near zero, as it has been reported before (Kong *et al.* 2021; Bertagna Silva *et al.* 2022). VEN was degraded by 40% and DV reached nearly 90% of degradation.

Table 2 shows the TPs identified in all the performed UV-C photolysis experiments. Some of them were different from the ones presented in Table 1, concerning UV-A photocatalysis. No TP was found for TMP. The MS² spectra for the compounds can be seen in Supplementary Figures S3–S5. The authors assume byproducts formed uniquely during photocatalysis were the result of reactions involving ROS species such as the hydroxyl radicals, since these are absent in photolysis.

Table 2 | TPs formed by UV-C photolysis in MQ water

TP	Parent compound	<i>m/z</i> (M + H ⁺)	RT (min)	Chemical formulae	Mass error (ppm)	Reaction	Identification confidence	Ref.
DV	VEN	264.195	2.081	C ₁₆ H ₂₅ NO ₂	-1.13	DM	Confirmed structure	Lajeunesse <i>et al.</i> (2012) and Osawa <i>et al.</i> (2019)
V-4	VEN	264.195	2.607	C ₁₆ H ₂₅ NO ₂	-1.25	DM	Probable structure	Osawa <i>et al.</i> (2019)
V-5	VEN	294.206	2.261	C ₁₇ H ₂₇ NO ₃	-1.10	H	Tentative candidate	Osawa <i>et al.</i> (2019)
V-6	VEN	292.190	2.488	C ₁₇ H ₂₅ NO ₂	-1.24	O	Tentative candidate	Osawa <i>et al.</i> (2019)
D-1	DV	280.019	1.674	C ₁₆ H ₂₅ NO ₃	-1.22	O	Tentative candidate	García-Galán <i>et al.</i> (2016)
D-4	DV	250.180	1.306	C ₁₅ H ₂₃ NO ₃	-1.12	D	Tentative candidate	García-Galán <i>et al.</i> (2016)

RT, retention time; O, oxidation; H, hydroxylation; DM, demethylation; DS, desaturation; DH, dehydration.

The monitoring of the TPs formation by UV-C photolysis is presented in Supplementary Figure S8. In comparison to Supplementary Figure S6, it can be seen that the TPs generated by the photolytic process in MQ water had smaller areas.

Figure 3 shows the proposed degradation pathways and TPs formation by means of UV-C photolysis for VEN and DV. Analysing the degradation of VEN, it is possible to see that, additionally to DV, its isomer *n*-

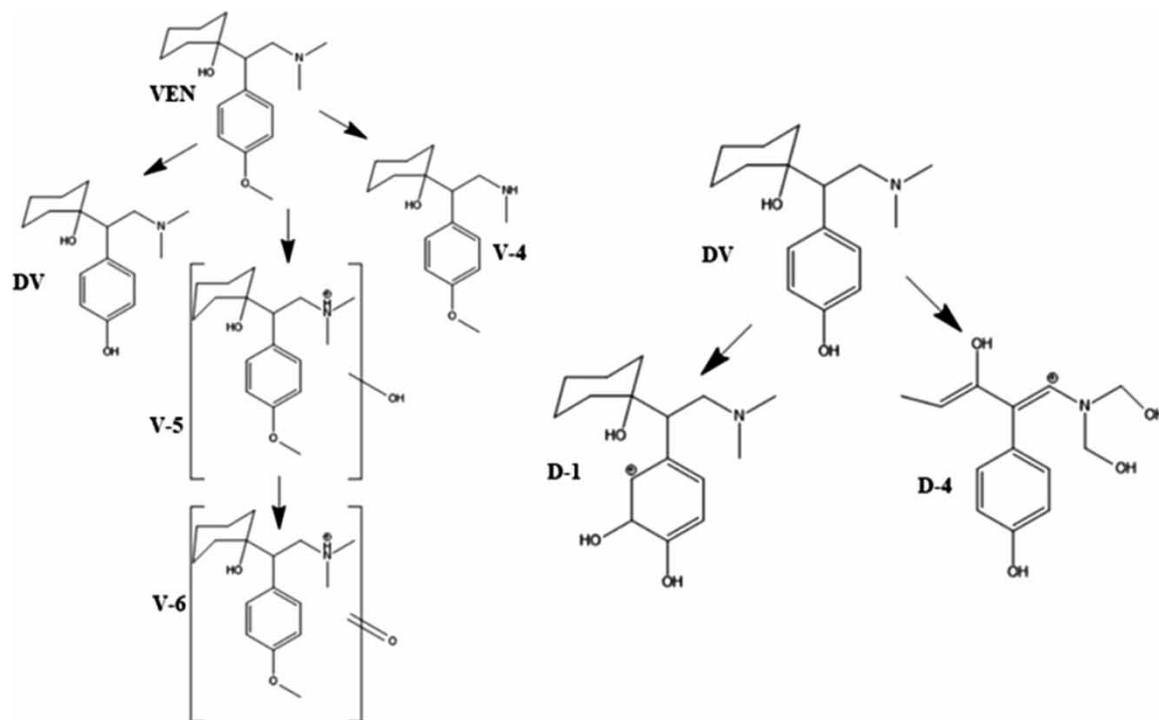


Figure 3 | Proposed TPs by UV-C photolysis.

desmethylvenlafaxine (V-4) was detected by the software as a probable structure. V-5 and V-6 were the result of hydroxylation and oxidation steps caused by the UV-C rays (Lambropoulou *et al.* 2017). The final amount of DV formed compared to UV-A photocatalysis was smaller.

On the other hand, the analysis of DV shows a larger formation of the TP D-1 for UV-C photolysis in comparison to UV-A photocatalysis (Figure 2). The formation of D-4 indicates that UV-C photolysis was able to break the cyclohexane ring of DV, which was not detected during UV-A photocatalysis.

4. CONCLUSIONS

In this work, UV-LED-based processes for the degradation of CECs and their respective TP formation were investigated. UV-A photocatalysis was capable of degrading, at least partially, the three target pollutants. After 6 h of reaction in MQ water, in fact, TMP was completely degraded, while VEN and DV reached 53 and 73% of removal, respectively. The results changed when tap water was used as a matrix, as well as when the chosen process was UV-C photolysis, since the compounds responded differently to the new conditions.

A new TP for venlafaxine was found (1-[2-(dimethylnitroaryl)-1-(4-methoxyphenyl)ethyl]cyclohexanol). No different pathways were observed when comparing MQ and tap water matrices for UV-A photocatalysis, although the peak areas of the TPs formed changed. When comparing UV-C photolysis with UV-A photocatalysis performed in MQ water, distinct pathways and different reaction mechanisms were proposed. Byproducts formed uniquely during photocatalysis were the result of reactions involving ROS species such as the hydroxyl radicals, since these are absent in photolysis.

Most of the TPs remained in the solution after 6 h of photodegradation and all of them had higher or similar molecular masses in comparison to the corresponding parent compounds and complete mineralization was, hence, not obtained. Whenever possible, their use should be limited and the replacement with less harmful compounds should be sought.

ACKNOWLEDGEMENTS

G.B. and M.J.F. acknowledge the Spanish State Research Agency of the Spanish Ministry of Science, Innovation and Universities for the Grant to the Creation of a permanent position Ramon y Cajal 2014 (RYC-2014-16754 and RyC-2015-17108, respectively). ICRA researchers thank funding received from the Economy and Knowledge

Department of the Catalan Government through Consolidated Research Groups (ICRA-ENV 2021 SGR 01282 and ICRA-TiA 2021 SGR 01283), as well as from the CERCA program. The Orbitrap™ system receives support from I-CERCA through CERCAGINYS program funded by MICINN.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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First received 15 June 2023; accepted in revised form 8 August 2023. Available online 19 August 2023