

Direct photolysis at 184.9 nm: An underestimated pathway for organic micropollutant removal during VUV/UV treatment

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ABSTRACT

Vacuum UV (VUV, 184.9 nm)/UV (253.7 nm) irradiation is increasingly investigated for the removal of organic micropollutants (OMPs) from water. Commonly, degradation during VUV/UV treatment is attributed to hydroxyl radical (HO[•])-mediated reactions, while the relative importance of direct VUV photolysis is assumed to be negligible. Here, we introduce and apply a novel methodology that differentiates and resolves the individual contributions of direct VUV photolysis, UV photolysis, and radical-induced degradation. Using controlled radical scavenging conditions, we systematically assessed degradation pathways for twenty representative OMPs. Direct VUV photolysis was found to constitute a substantial fraction of total removal. Under conditions suppressing radical reactions, VUV photolysis was estimated to be 63% and 25% of the total degradation of 1H-benzotriazole and paracetamol, respectively. Even under conditions favoring radical-induced degradation, VUV photolysis remained measurable and, for several compounds, non-negligible. The contribution of secondary radical species was additionally evaluated to refine mechanistic interpretation. Experiments conducted in tap water and canal water confirmed the relevance of VUV photolysis under realistic water matrices. These findings demonstrate that direct VUV photolysis represents a significant and currently underestimated pathway in VUV/UV treatment. The proposed methodology improves pathway-level mechanistic resolution and provides experimental evidence to inform future kinetic modeling and reactor design strategies in VUV-based water treatment.

1. Introduction

Organic micropollutants (OMPs) in water pose challenges for water treatment and water reuse quality, and ultraviolet (UV)-based Advanced Oxidation Processes (AOPs) have been proven effective in degrading these contaminants [1,2]. One of the obvious disadvantages of UV-based AOPs is the dependence on oxidants, e.g., H₂O₂ and Cl₂, to generate radicals, e.g., hydroxyl radical (HO[•]) and chloride radical (Cl[•]). Despite their demonstrated effectiveness in OMPs degradation, this reliance on chemical oxidants can generate undesired byproducts, necessitate additional post-treatment steps, and increase both energy and operational expenditures [3]. A promising, chemical-free alternative is to incorporate vacuum UV (VUV) irradiation, particularly at 184.9 nm, into the processes [4,5]. The VUV at 184.9 nm directly breaks down the water molecule bonds to produce various reactive species, including

HO[•], solvated electron (e_{aq}⁻), and hydrogen radical (H[•]), without requiring external oxidants to initiate AOPs for OMPs abatement [6]. Previous investigations show the effectiveness of the VUV/UV process for degrading OMPs across diverse water matrices, using both batch and flow-through reactors, facilitating further exploration of its application potential in water treatment [7–11]. Dubowski et al. [10] applied VUV/UV processes to remove carbamazepine from groundwater, surface water, and tertiary treated wastewater; when combined with electro-dialysis as pretreatment, natural organic matter and ions were significantly reduced, resulting in enhanced carbamazepine removal. Shi et al. [9] and Matsushita et al. [8] investigated the degradation of 1,4-dioxane under VUV/UV irradiation in groundwaters, river water, and dechlorinated tap water using batch experiments, and further simulated its removal in flow-through photoreactors using computational fluid dynamics models. George et al. [7] evaluated the degradation of an OMPs

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mixture in reverse osmosis permeate, drinking waters, and secondary wastewater effluent, offering insights into the scale-up of VUV/UV systems by interpreting laboratory results through a useful-absorbed-energy-based figure of merit. Furthermore, commercial mercury-based lamps inherently emit both UV at 253.7 nm and VUV at 184.9 nm radiation. With modifications to quartz sleeves and lamps, VUV processes could be integrated into existing water treatment schemes, potentially reducing chemical dosage and associated costs. Lu et al. [12] evaluated five types of quartz sleeves and illustrated that enhanced VUV intensity, achieved through sleeve modification, resulted in higher trimethoprim degradation and lower electrical energy per order (E_{EO}) of degradation. Additionally, Wang et al. [13] demonstrated the degradation of eight OMPs in VUV/UV treatment and quantified the H_2O_2 savings in different light pathlengths relative to conventional UV/ H_2O_2 processes.

Current mechanistic research on VUV/UV processes for OMPs removal has primarily focused on the radical-induced pathways, particularly $HO^\bullet$ -induced AOP, owing to its strong and non-selective capability. In addition, the use of reducing reactive species, e.g., e_{aq}^- , has been explored for the treatment of halogenated compounds [14,15]. Conversely, the contribution of direct photolysis at 184.9 nm is often directly ignored due to the shallow penetration of VUV photons caused by the high absorption of water and dissolved inorganic constituents [16,17]. However, experimental observation indicated that when high concentrations of $HO^\bullet$ scavengers, e.g., tert-butyl alcohol (TBA) and methanol, are introduced to effectively shield $HO^\bullet$ -mediated oxidation, OMPs continued to degrade [13,18,19]. This observation suggests that direct photolysis at 184.9 nm may play a more significant role than previously recognized. Moreover, direct VUV photolysis has recently been reported to contribute to the degradation of highly recalcitrant PFAS, highlighting the importance of quantifying its role in the removal of other OMPs [20]. In this study, we systematically examined the roles of three degradation pathways—radical-induced degradation, direct photolysis at 184.9 nm (VUV photolysis), and direct photolysis at 253.7 nm (UV photolysis)—in the abatement of OMPs during VUV/UV treatment. The significance of direct photolysis, especially VUV photolysis, was evaluated under the conditions where radical-induced degradation was selectively suppressed in a controlled manner by introducing radical scavengers. High VUV absorbance induced by inorganic anions (e.g., Cl^-) was avoided to prevent added complexities in assessing the relative contribution of VUV photolysis.

Furthermore, recent mechanistic studies have concentrated on individual compounds with limited attention to the complexity of realistic water matrices. In waters containing high levels of organics, e.g., other contaminants or natural organic matter, the balance among different degradation pathways during VUV/UV processes may shift. Organic constituents primarily act as radical scavengers, substantially reducing the availability of radicals for OMP degradation, and to a lesser extent, they also compete for VUV photons. Additionally, the susceptibility of individual OMPs to absorption of VUV photons varies widely, further influencing their degradation performance. In this study, a mixture of twenty pharmaceuticals and pesticides with varying susceptibilities to UV photolysis was selected to represent a broad range of commonly detected OMPs in surface waters and to assess the contribution of direct VUV photolysis under various scavenging scenarios. Moreover, the influence of secondary radicals on the assessment of VUV photolysis was investigated through experiments in which scavengers for secondary radicals were introduced and dissolved oxygen (DO) was removed to limit scavenging of reducing reactive species [14,21,22]. Canal water and tap water were also tested to assess the implications of VUV processes in realistic matrices and to provide insight into OMPs abatement when organics and anions compete for VUV photons.

In this work we develop and apply a methodology that differentiates between VUV photolysis, UV photolysis, and radical-induced degradation within a single VUV/UV system. While previous studies have focused predominantly on radical chemistry, a systematic assessment of direct VUV photolysis across a broad spectrum of OMPs has not been

reported. By resolving these concurrent mechanisms at the pathway level, this experimental study advances the understanding of VUV/UV processes and provides mechanistic evidence to inform future kinetic modeling and photoreactor design for chemical-free VUV-based water treatment.

2. Materials and methods

2.1. Chemicals and analytical methods

Twenty OMPs were selected to evaluate the contribution of direct VUV photolysis to their degradation. Paracetamol, 1H-benzotriazole, atrazine, bezafibrate, carbamazepine, diclofenac (sodium), diuron, furosemide, gemfibrozil, hydrochlorothiazide, ibuprofen, isoproturon, ketoprofen, metoprolol (tartrate), N,N-diethyl-m-toluamide (DEET), nadolol, antipyrine, propranolol (hydrochloride), sulfamethoxazole, and trimethoprim were purchased from Sigma Aldrich. Stock solutions of individual OMP and cocktail solutions were prepared in milli-Q water. The initial concentration for each OMP in the cocktail solution was $0.06 \mu\text{mol L}^{-1}$. All solutions were stored at 4°C and returned to room temperature before the experiment. The solution pH was not adjusted and measured 5.6 before treatment (METTLER TOLEDO SevenExcellence™). TBA concentrations of 7.00, 1.00, 0.40, 0.20, 0.11, 0.07, and 0.05 mmol L^{-1} were used to simulate various $HO^\bullet$ scavenging conditions. The scavenging impact of twenty OMPs was expressed as an equivalent TBA concentration based on their reaction rates with $HO^\bullet$ (Table S2.1). Hereafter, scavenging concentration refers to the sum of added and equivalent TBA concentrations. The sample exposure times were 30, 60, 90, 150, 210, 270, and 300 s in all experiments. Experiments were performed in duplicate for each reaction time. Canal water from a drainage canal and tap water were collected in Leeuwarden, the Netherlands.

Chemical analyses of all OMPs were performed with a triple quadrupole liquid chromatography mass spectrometer (LC-MS/MS) (Agilent Technologies). An Agilent Zorbax Eclipse Plus C18 RRHD column ($1.8 \mu\text{m}$, $50 \times 2.1 \text{ mm}$) with a UHPLC guard Zorbax Eclipse Plus C18 pre-column ($1.8 \mu\text{m}$, 2.1 mm , Agilent Technologies) was used for separation. The analysis used a binary pump with an isocratic mobile phase of 60% aqueous buffer (10 mmol L^{-1} ammonia, 10.4 mmol L^{-1} formic acid, and 0.04 mmol L^{-1} oxalic acid) and 40% acetonitrile at a flow rate of 0.25 mL min^{-1} over a 5-min runtime. MassHunter software was used to process data.

2.2. Collimated beam setup

All degradation experiments were conducted in a collimated beam apparatus equipped with a low-pressure amalgam UV/VUV lamp (M1-AK-242, Trojan Technologies, Canada). The UV fluence rate at 253.7 nm incident on the reactor surface was measured as $6.5 \times 10^{-4} \text{ W cm}^{-2}$, using a NIST Traceable Light Measurement System from International Light Technologies. The fluence rate of 184.9 nm radiation was determined to be $1.2 \times 10^{-4} \text{ W cm}^{-2}$ using actinometry with carbamazepine as the reference probe compound (SI 1.1) and its stability was independently monitored using a NIST Traceable Light Measurement System during the experiments. The depth of the reactor cell was 10 mm (cylindrical quartz cell, Starna Scientific). A magnetic stirrer was used in the reactor cell to create a perfect mixing condition. N_2 gas was constantly purged into the lamp chamber and collimator to eliminate the air.

2.3. Degradation experiment and kinetic data analysis

Across the entire range of TBA concentrations tested, the degradation of each OMP (C/C_0) during VUV/UV treatment followed pseudo-first-order kinetics with respect to total absorbed energy (Eq. 1) [23], characterized by an overall degradation rate constant (k , $\text{m}^3 \text{ J}^{-1}$). The

derivation of this pseudo-first-order expression and the rationale for using energy-based degradation kinetics are provided in SI 1.2 and 1.3. Degradation of an OMP under VUV/UV radiation can proceed via three pathways: radical-induced degradation, VUV photolysis, and UV photolysis. Accordingly, the overall degradation rate constant (k) was expressed as the sum of contributions from these pathways (Eq. 2), including k'_{radical} (mol J^{-1}), k'_{UV} ($\text{m}^3 \text{J}^{-1}$), and k'_{VUV} ($\text{m}^3 \text{J}^{-1}$). The dependence of k on scavenger concentration (S , mol m^{-3}) reflects the suppression of radical-induced degradation by TBA. As described in SI 1.2, the steady-state $\text{HO}^\bullet$ concentration decreases as the scavenger concentration increases, reducing the radical-induced contribution to the overall degradation in proportion to $1/S$. In contrast, k'_{UV} and k'_{VUV} are independent of scavenging conditions and are intrinsic to the photochemical properties of the target OMPs. The factor 1000 accounts for the conversion from liters to cubic meters.

To determine the k'_{radical} , k'_{UV} , and k'_{VUV} , exponential regression using Eq. 3, which was derived from Eq. 1 and 2, was performed using RStudio (version 2024.12.1, SI 1.4). The variable inputs to the regression analysis were total absorbed energy (AE , J m^{-3}), the reciprocal of various scavenger concentrations ($1/S$, $\text{m}^3 \text{mol}^{-1}$), and the normalized OMP concentration (C/C_0) obtained under each scavenging condition. Besides, radiation type was included as a categorical variable where $\text{lamp} = 1$ indicated illumination with VUV/UV radiation, while $\text{lamp} = 0$ represented UV radiation only. When $\text{lamp} = 0$, VUV radiation was experimentally blocked using an additional quartz cell filled with a 5 mmol L^{-1} NaCl solution, which was placed above the experimental cell. The incident VUV irradiance was confirmed to be zero in the presence of the NaCl cell. A correction factor of 1.09, determined under the same collimated beam conditions, was applied to account for UV losses due to reflections caused by the additional cell. Under sufficiently high scavenging conditions, corresponding to extrapolation of S to infinity, radical-induced degradation is strongly suppressed, and the overall degradation rate constant (k) of an OMP is dominated by direct UV and VUV photolysis (k'_{UV} and k'_{VUV} , Eq. 2). The individual contributions of radical-induced degradation, UV photolysis, and VUV photolysis to overall OMP removal were assessed under different scavenging conditions using their respective degradation rates.

$$\text{The overall degradation } \frac{C}{C_0} = e^{-k \cdot AE} \quad (1)$$

$$\text{The overall degradation rate constant } k = k'_{\text{radical}} \cdot \frac{1}{S \cdot 1000} + k'_{\text{UV}} + k'_{\text{VUV}} \quad (2)$$

$$\frac{C}{C_0} = a \cdot e^{-\left(k'_{\text{radical}} \cdot \frac{1}{S \cdot 1000} + \frac{k'_{\text{UV}}}{1 + 0.09 \cdot (1 - \text{lamp})} + k'_{\text{VUV}} \cdot \text{lamp}\right) \cdot AE} \quad (3)$$

The total absorbed energy (AE , J m^{-3}) was defined as the sum of the absorbed energy at 184.9 nm ($AE_{184.9\text{nm}}$, J m^{-3}) and 253.7 nm ($AE_{253.7\text{nm}}$, J m^{-3}) (Eq. 4). In a reactor cell with 1 cm pathlength, all incident radiation at 184.9 nm was absorbed, so $AE_{184.9\text{nm}}$ equals the incident fluence rate ($I_{a, 184.9\text{nm}}$, W m^{-2}) over the reactor pathlength (l , m) during a specific irradiation time (t , s) [7]. $I_{a, 184.9\text{nm}}$ was determined using actinometry (Section 2.2). Incident radiation at 253.7 nm was only partially absorbed. The absorbed radiation was calculated as the difference between the incident radiation and the transmitted radiation. As common for standardized collimated beam testing, the incident radiation on the cell surface (I_0 , 253.7nm , W m^{-2}) was corrected using the reflection factor ($RF = 0.975$), Petri factor ($PF = 0.973$), and divergence factor ($DF = 0.971$) to obtain the irradiance [7,24]. Because TBA and water molecules exhibit negligible absorption at 253.7 nm (Table S2.2), the absorbed energy at 253.7 nm ($AE_{253.7\text{nm}}$, J m^{-3}) corresponds solely to the absorption by the cocktail OMPs. The absorption coefficient of the cocktail solution at 253.7 nm ($a_{253.7}$, m^{-1}) was measured using a UV-VIS spectrophotometer (Shimadzu UV-1800).

$$AE = AE_{184.9\text{nm}} + AE_{253.7\text{nm}} = \left(\frac{I_{a, 184.9}}{l} + I_{0, 253.7} \cdot RF \cdot PF \cdot DF \cdot \frac{(1 - 10^{-a_{253.7}l})}{l} \right) \cdot t \quad (4)$$

2.4. Impact of secondary radicals

To investigate the impact of secondary radicals, namely $\text{O}_2^{\bullet-}$ and $\text{HO}_2^\bullet$, nitrogen (N_2) gas was purged into the solutions for 20 min before VUV/UV treatment to eliminate DO and carbon dioxide (CO_2). After purging N_2 , water samples were transferred to reaction cells inside a glove box to prevent air contact. The DO concentration after N_2 purging and subsequent treatment was measured using an oxygen dot sensor (Fibox 4 trace, PreSens Precision Sensing GmbH). Additionally, chloroform (CHCl_3 , 0.8 mmol L^{-1}) was used as a scavenger for $\text{O}_2^{\bullet-}$ [21]. The effects of either N_2 purging or CHCl_3 addition (hereafter referred to as categorical variable “condition”) on OMP degradation were evaluated respectively using Eq. 5, where “condition” is a binary variable. When neither N_2 purging nor CHCl_3 addition was applied, the condition was set to 0, such that Eq. 5 simplifies to Eq. 1. Under this condition, data were collected as described in 2.3, and the degradation rate solely responded to parameters b . When N_2 gas was purged or CHCl_3 was added, the condition was set to 1, the change of degradation rate was described by parameters c . The pre-exponential factor a accounts for minor deviations of the initial normalized concentration from unity. A condition was deemed to have a significant impact on OMP degradation if it showed statistical significance ($p\text{-value} \leq 0.05$) and if $|c|/|b| \geq 0.1$.

$$\frac{C}{C_0} = a \cdot e^{-(b + c \cdot \text{condition}) \cdot AE} \quad (5)$$

3. Results

3.1. Degradation kinetics of twenty OMPs under various scavenging conditions

Twenty OMPs were ranked based on their UV sensitivity, characterized by their molar absorption coefficients and quantum yields at 253.7 nm (Table S2.1). Four representative OMPs—isoproturon, 1H-benzotriazole, atrazine, and diclofenac—were selected to present UV-resistant (low UV sensitivity), UV-neutral (medium UV sensitivity), and UV-sensitive (high UV sensitivity) categories. For UV-resistant OMP, e.g., isoproturon, UV photolysis minimally contributed to OMP abatement (Table 1), with a fitted UV photolysis rate constant of $0.404 \times 10^{-6} \text{ m}^3 \text{J}^{-1}$. Isoproturon abatement was dominated by radical-induced degradation and VUV photolysis. The overall degradation rate decreased from $95.1 \times 10^{-6} \text{ m}^3 \text{J}^{-1}$ to $5.83 \times 10^{-6} \text{ m}^3 \text{J}^{-1}$ as TBA concentrations increased from 0.05 to 7.00 (mmol L^{-1}) (Fig. 1a). For UV-neutral OMPs, 1H-benzotriazole and atrazine exhibited UV photolysis rate constants of $2.90 \times 10^{-6} \text{ m}^3 \text{J}^{-1}$ and $3.48 \times 10^{-6} \text{ m}^3 \text{J}^{-1}$, respectively (Table 1). Despite higher contribution from UV photolysis, radical-induced degradation and VUV photolysis were the predominant pathways in removing UV-neutral OMPs. However, the overall degradation rate constants of 1H-benzotriazole were less affected by TBA concentrations, decreasing from $137 \times 10^{-6} \text{ m}^3 \text{J}^{-1}$ to $68.6 \times 10^{-6} \text{ m}^3 \text{J}^{-1}$ as TBA concentrations elevated from 0.05 to 7.00 (mmol L^{-1}) (Fig. 1b). In contrast, atrazine removal was lower but demonstrated a stronger dependence on TBA concentrations, with rate constants decreasing from $35.8 \times 10^{-6} \text{ m}^3 \text{J}^{-1}$ to $4.75 \times 10^{-6} \text{ m}^3 \text{J}^{-1}$ across the same TBA gradient. The different trends for atrazine and 1H-benzotriazole indicated the greater contribution of radical-induced degradation in atrazine removal compared to 1H-benzotriazole. For UV-sensitive OMPs, diclofenac presented a high UV photolysis rate constant of $4.03 \times 10^{-5} \text{ m}^3 \text{J}^{-1}$ (Table 1). Similarly, other UV-sensitive compounds (Fig. S3.1), e.g., ketoprofen, sulfamethoxazole, and antipyrine, showed relatively high UV photolysis rate constants in the range of 10^{-5} – $10^{-4} \text{ m}^3 \text{J}^{-1}$. Notably,

Table 1

The UV photolysis, VUV photolysis, and radical-induced degradation rate constants of twenty OMPs were determined by fitting the experimental data to Eq. 3. The total direct photolysis was the sum of VUV photolysis and UV photolysis rate constants. Uncertainties are reported as 95% confidence intervals (R, confint() function). The uncertainty of total direct photolysis was propagated from the uncertainties of UV photolysis and VUV photolysis: $\sqrt{([UV \text{ photolysis}]^2 + [VUV \text{ photolysis}]^2)}$.

OMP	$k_{VUV} (\times 10^{-6} \text{ m}^3 \text{ J}^{-1})$	$k_{UV} (\times 10^{-6} \text{ m}^3 \text{ J}^{-1})$	$k_{\text{total direct photolysis}} (\times 10^{-6} \text{ m}^3 \text{ J}^{-1})$	$k_{\text{radical}} (\times 10^{-6} \text{ mol J}^{-1})$
1H-Benzotriazole	66.1 ± 1.8	2.90 ± 0.61	69.1 ± 1.9	4.80 ± 0.33
Furosemide	16.7 ± 2.5	1.10 ± 1.86	17.8 ± 3.0	6.08 ± 0.60
Paracetamol	15.4 ± 2.0	0.00 ± 1.61	15.4 ± 2.6	4.52 ± 0.41
Diclofenac	14.9 ± 1.58	40.3 ± 1.2	55.2 ± 2.0	7.05 ± 0.27
Ibuprofen	8.16 ± 1.46	0.00 ± 1.25	8.16 ± 1.92	5.15 ± 0.30
Bezafibrate	7.41 ± 0.76	0.356 ± 0.654	7.77 ± 1.00	5.47 ± 0.16
Antipyrine	5.62 ± 1.16	12.4 ± 1.0	18.0 ± 1.5	3.65 ± 0.17
Isoproturon	5.55 ± 0.60	0.404 ± 0.525	5.95 ± 0.80	5.84 ± 0.13
Sulfamethoxazole	5.39 ± 1.56	35.6 ± 1.3	41.0 ± 2.0	5.84 ± 0.25
Metoprolol	3.19 ± 0.69	0.00 ± 0.62	3.19 ± 0.93	5.19 ± 0.14
Trimethoprim	2.97 ± 0.86	0.00 ± 0.78	2.97 ± 1.16	5.47 ± 0.18
Gemfibrozil	2.32 ± 1.18	0.00 ± 1.08	2.32 ± 1.59	5.18 ± 0.23
Atrazine	2.30 ± 0.62	3.48 ± 0.58	5.79 ± 0.85	1.87 ± 0.06
Nadolol	2.22 ± 0.64	0.00 ± 0.59	2.22 ± 0.87	5.21 ± 0.13
Diuron	1.87 ± 0.73	5.59 ± 0.66	7.46 ± 0.99	4.86 ± 0.13
Carbamazepine	1.46 ± 0.66	0.00 ± 0.60	1.46 ± 0.89	6.24 ± 0.15
Hydrochlorothiazide	1.24 ± 0.57	2.91 ± 0.53	4.15 ± 0.78	3.66 ± 0.08
DEET	1.08 ± 0.56	0.00 ± 0.52	1.08 ± 0.76	4.42 ± 0.10
Propranolol	0.762 ± 0.962	1.27 ± 0.88	2.03 ± 1.30	6.69 ± 0.23
Ketoprofen	0.00 ± 19.33	361 ± 16	361 ± 25	5.61 ± 1.50

ketoprofen degradation was primarily driven by UV irradiation, with overall degradation rate constants remaining at $3.85 \pm 0.50 (\times 10^{-4} \text{ m}^3 \text{ J}^{-1})$, regardless of TBA concentrations. The degradation kinetics of the sixteen other OMPs are presented in Fig. S3.1.

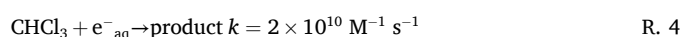
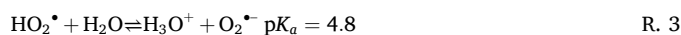
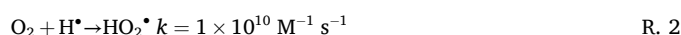
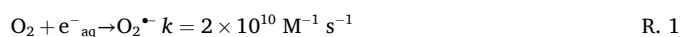
3.2. Degradation pathways under VUV/UV radiation

The primary degradation pathways for an OMP in VUV/UV processes include $\text{HO}^\bullet$ -induced radical-induced degradation, VUV photolysis, and UV photolysis. The rate constants of these degradation pathways were determined using Eq. 3 and are summarized in Table 1. The radical-induced degradation rate constant was dependent on the scavenger concentration, specifically the $\text{HO}^\bullet$ scavenger in this study. In contrast, the VUV and UV photolysis rate constants were not affected by scavenger conditions because TBA exhibits negligible absorption of both UV and VUV radiation (Table S2.2), indicating that photolysis rate constants depend solely on the inherent photochemical properties of the OMPs. The total direct photolysis rate constants were represented by the conditions where high scavenging conditions effectively suppressed radical-induced degradation. Among the twenty OMPs evaluated, 1H-benzotriazole and diclofenac exhibited relatively high total direct photolysis rate constants of $69.1 \times 10^{-6} \text{ m}^3 \text{ J}^{-1}$ and $55.2 \times 10^{-6} \text{ m}^3 \text{ J}^{-1}$, respectively (Table 1). 1H-benzotriazole, identified as a UV-neutral OMP, showed a low UV photolysis rate constant of $2.90 \times 10^{-6} \text{ m}^3 \text{ J}^{-1}$, indicating that VUV photolysis contributed more than 95% of total direct photolysis and could play a crucial role in its removal. In contrast, diclofenac, a UV-sensitive OMP, displayed a high UV photolysis rate constant of $40.3 \times 10^{-6} \text{ m}^3 \text{ J}^{-1}$. Consequently, UV photolysis was the primary contributor to total direct photolysis in diclofenac degradation, whereas the contribution of VUV photolysis was comparatively smaller, accounting for 27%. Isoproturon and atrazine showed low total direct photolysis rate constants of $5.95 \times 10^{-6} \text{ m}^3 \text{ J}^{-1}$ and $2.86 \times 10^{-6} \text{ m}^3 \text{ J}^{-1}$ (Fig. 2), respectively, with little VUV photolysis. Although atrazine has a high molar absorption coefficient at 184.9 nm, it exhibits a low quantum yield, confirming that VUV photolysis plays only a minor role in its removal and that radical-induced degradation is the dominant pathway [25]. Ketoprofen had the highest total direct photolysis rate constant, primarily due to UV photolysis, aligning well with both the UV sensitivity calculations (Table S2.1) and experimental observations (Fig. S3.1). Similarly, sulfamethoxazole showed high total direct photolysis and UV photolysis rate constants, but its VUV photolysis rate constant should not be overlooked and could be substantially crucial

under high scavenging conditions. Notably, twelve OMPs demonstrated higher VUV photolysis rate constants compared to UV photolysis, particularly among UV-resistant compounds, such as paracetamol and DEET, implying the critical role of VUV photolysis in OMP removal.

3.3. Impact of dissolved oxygen and superoxide radical

When evaluating the radical-induced degradation pathways, $\text{HO}^\bullet$ was the primary focus and TBA was used to regulate the $\text{HO}^\bullet$ steady-state concentrations. However, other radicals, e.g., $\text{O}_2^{\bullet-}$ and $\text{HO}_2^\bullet$, could be generated and participate in OMP abatement [26]. The impact of these secondary radicals could be misinterpreted as direct photolysis, leading to an overestimation of the contribution of VUV photolysis. Notably, under the default experimental conditions (only TBA), e_{aq}^- and/or $\text{H}^\bullet$ generated from water photolysis would not introduce inaccuracies into the assessment of VUV photolysis, as DO effectively scavenges e_{aq}^- and $\text{H}^\bullet$. As a result, $\text{O}_2^{\bullet-}$ and $\text{HO}_2^\bullet$ are formed, introducing uncertainty in evaluating the contribution of VUV photolysis (R. 1 and R. 2) [27]. At pH 5.6, which exceeds the pKa of 4.8, the equilibrium favors the formation of $\text{O}_2^{\bullet-}$ over $\text{HO}_2^\bullet$ (R. 3). To assess the impact of $\text{O}_2^{\bullet-}$ and $\text{HO}_2^\bullet$, N_2 gas was purged through the samples prior to treatment to eliminate DO, while 7.00 mmol L^{-1} TBA was added to minimize $\text{HO}^\bullet$ -mediated oxidation. Correspondingly, DO concentrations were reduced to $2.09 \pm 0.23 \text{ mg L}^{-1}$ (Table S2.3). Under the N_2 purging condition, $\text{O}_2^{\bullet-}$ and $\text{HO}_2^\bullet$ formations were limited while $\text{HO}^\bullet$ was scavenged by TBA. In contrast, e_{aq}^- and $\text{H}^\bullet$ persisted in solution due to the lack of DO and their low reaction rate constants with TBA ($k_{\text{e}_{\text{aq}}^-} < 4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$; $k_{\text{H}^\bullet} = 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) [22,28]. Additionally, chloroform (CHCl_3) was introduced under aerated conditions in the presence of 7.00 mmol L^{-1} TBA as an effective scavenger of both $\text{O}_2^{\bullet-}$ and e_{aq}^- (R. 4 and 5) [22,29]. Purging N_2 gas or adding CHCl_3 was set as a categorical variable (noted as “condition”) in Eq. 5 to evaluate the impact of secondary radicals on the overall degradation rate constants of OMPs.



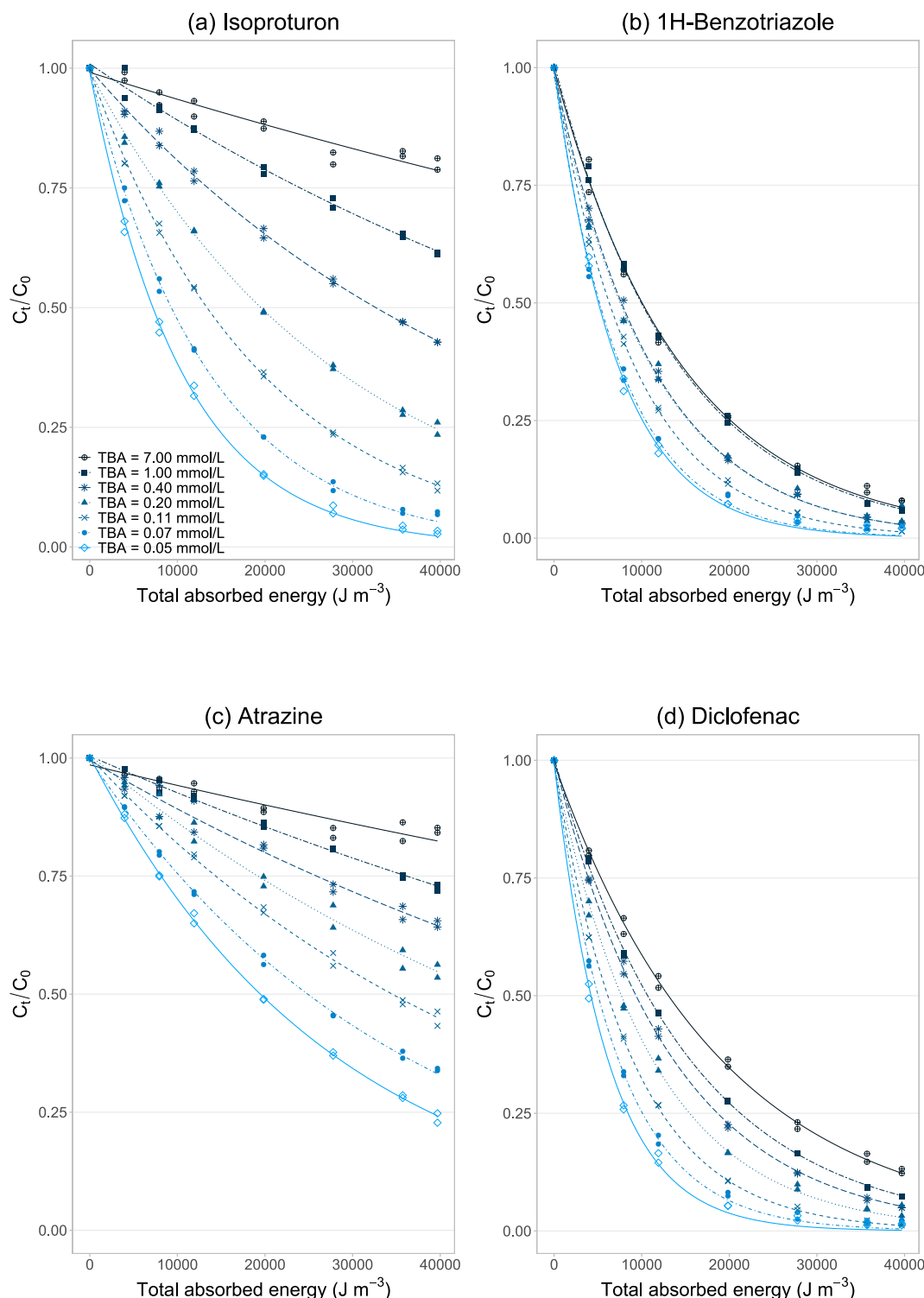
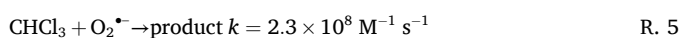


Fig. 1. Degradation of isoproturon, 1H-benzotriazole, atrazine, and diclofenac at varying TBA concentrations under VUV/UV radiation. Initial concentration $0.06 \mu\text{mol L}^{-1}$ for each OMP, initial pH 5.6.



The degradation rates of atrazine, diuron, diclofenac, hydrochlorothiazide, DEET, propranolol, bezafibrate, and isoproturon were not influenced by purging N_2 gas or adding CHCl_3 , indicating little contribution from secondary radicals (Table 2 and Fig. S3.2). In contrast, the degradation rates of 1H-benzotriazole, ketoprofen, paracetamol, and trimethoprim decreased with both N_2 purging and CHCl_3 addition (Fig. 2 and Table 2), suggesting the involvement of $\text{O}_2^{\bullet-}$ and/or $\text{HO}_2^{\bullet}$ in

their removal [29]. This indicates that their degradation induced by VUV photolysis may have been previously overestimated. Conversely, the removal rates of ibuprofen, metoprolol, and nadolol declined upon CHCl_3 addition but showed little response to N_2 purging, indicating potential contributions from $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ and $\text{e}_{\text{aq}}^-/\text{H}^{\bullet}$ (Table 2). The presence of either $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ or $\text{e}_{\text{aq}}^-/\text{H}^{\bullet}$ group independently may be sufficient to sustain the removal, compensating for the absence of the other. Furthermore, sulfamethoxazole degradation decreased under N_2

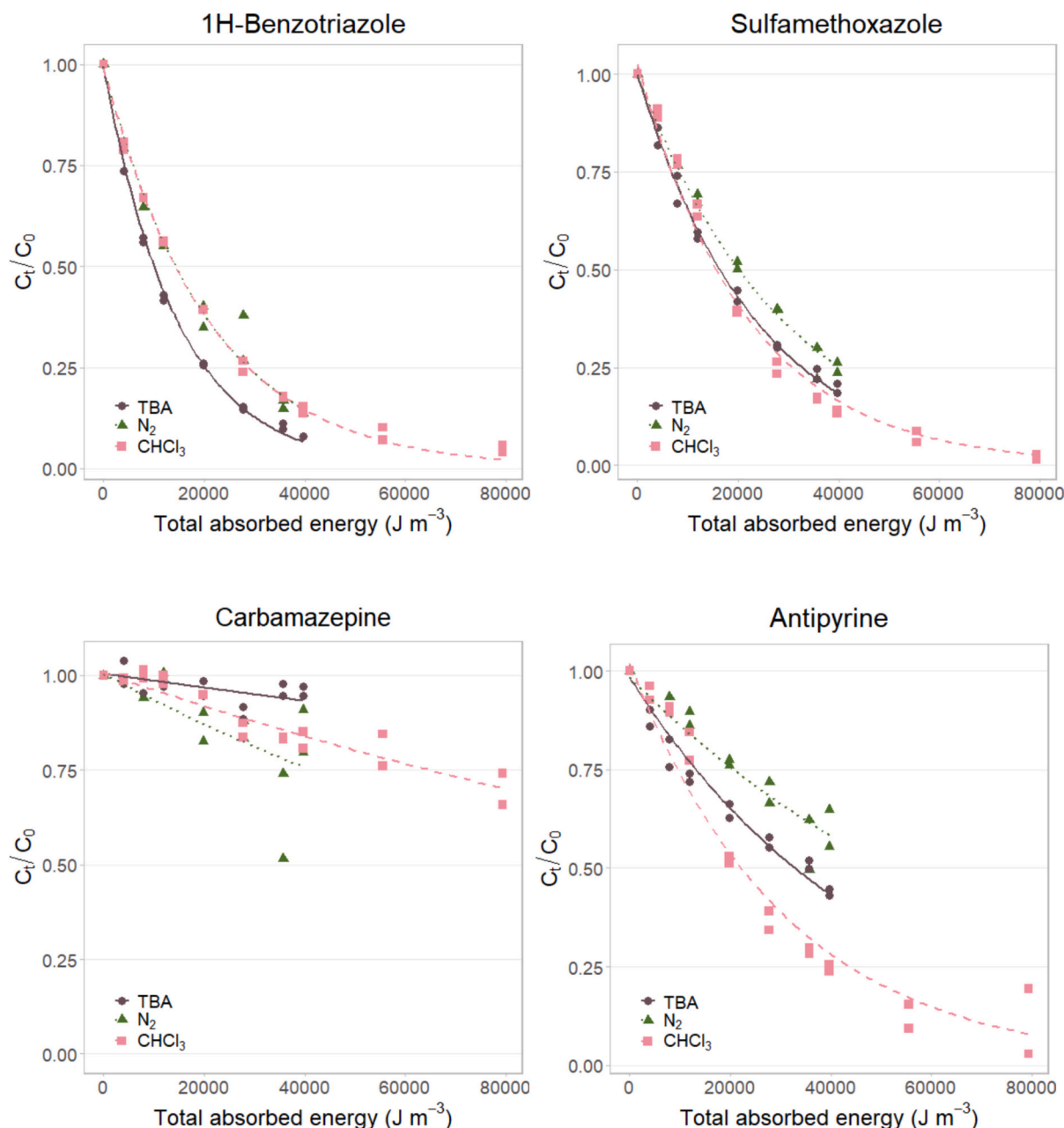


Fig. 2. The degradation of 1H-benzotriazole, sulfamethoxazole, carbamazepine, and antipyrine with TBA addition, N_2 purging, and CHCl_3 addition. In all experiments, 7.00 mmol L^{-1} TBA was added. Data points deviating by more than three standard deviations from the mean were considered outliers and excluded from further analysis. Variability of data points in N_2 purging condition was mainly attributed to fluctuations in initial DO.

purging but remained unaffected by CHCl_3 addition (Fig. 2), indicating the involvement of e_{aq}^- and/or $\text{H}^\bullet$. Carbamazepine abatement improved under both N_2 purging and CHCl_3 addition (Fig. 2), likely due to the higher availability of e_{aq}^- and/or $\text{H}^\bullet$ under both conditions [30]. In the case of ibuprofen, metoprolol, nadolol, sulfamethoxazole, and carbamazepine, further research is necessary to clarify the roles of $\text{O}_2^-/\text{HO}_2^\bullet$ and $e_{\text{aq}}^-/\text{H}^\bullet$ in their degradation. Additionally, the degradation rates of furosemide, antipyrine (Fig. 2), and gemfibrozil increased in the presence of CHCl_3 (Table 2), potentially due to the generation of alternative radicals from CHCl_3 [31]. According to Razavi et al. [32], gemfibrozil and bezafibrate have high reaction rates with e_{aq}^- ($k_{\text{bezafibrate}} = 11.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$; $k_{\text{gemfibrozil}} = 6.26 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), but, in our experiments, decreasing the DO concentration did not enhance their removal.

Secondary radicals generated during the VUV/UV process, specifically O_2^- and $\text{HO}_2^\bullet$, could react with target OMPs, leading to an

overestimation of the contribution of VUV photolysis to overall OMP degradation if their effects are not properly accounted for. However, completely eliminating the influence of all radicals under VUV/UV irradiation is nearly impossible because introducing radical scavengers can also lead to the formation of new radicals. In this study, limited influence of secondary radicals was observed for the majority of compounds (Table 2), supporting the robustness of the approach in distinguishing the contribution of VUV photolysis.

4. Discussion

4.1. Contribution of VUV photolysis to OMPs degradation

In a perfectly mixed system, OMP concentrations were assumed to be homogeneously distributed throughout the volume, while $\text{HO}^\bullet$

Table 2

The impact of N₂ purging or CHCl₃ addition on OMP degradation. The asterisk (*) and its numbers indicate that the condition in Eq. 5 is statistically significant. ***: $p \leq 0.001$; **: $p \leq 0.01$; *: $p \leq 0.05$. The ratio c/b indicates the influence of the condition on OMP degradation: larger absolute values indicate a greater influence, with negative values signifying a negative impact and positive values indicating a positive impact. All experiments were conducted with a TBA concentration of 7.00 mmol L⁻¹.

OMP	Impact of purging N ₂ : ratio of c/b	Impact of adding CHCl ₃ : ratio of c/b	Secondary radicals possibly contribute to the degradation
Atrazine	0.162	0.00328	
Diuron	0.124	-0.0402	
Diclofenac	-0.111	-0.015	
Hydrochlorothiazide	0.429	-0.0651	
DEET	0.512	0.208	
Propranolol	0.429	-0.0597	
Bezafibrate	0.352	-0.0492	
Isoproturon	0.0771	0.0918	
1H-Benzotriazole	-0.299***	-0.297***	O ₂ ⁻ and/or HO ₂ ⁻
Ketoprofen	-0.188***	-0.180***	O ₂ ⁻ and/or HO ₂ ⁻
Paracetamol	-0.678***	-0.500***	O ₂ ⁻ and/or HO ₂ ⁻
Trimethoprim	-0.462*	-0.514**	O ₂ ⁻ and/or HO ₂ ⁻
Ibuprofen	-0.0474	-0.393*	O ₂ ⁻ /HO ₂ ⁻ and e _{aq} ⁻ /H ⁺
Metoprolol	0.145	-0.369**	O ₂ ⁻ /HO ₂ ⁻ and e _{aq} ⁻ /H ⁺
Nadolol	-0.184	-0.381***	O ₂ ⁻ /HO ₂ ⁻ and e _{aq} ⁻ /H ⁺
Sulfamethoxazole	-0.222***	0.045	e _{aq} ⁻ and/or H ⁺
Carbamazepine	2.85***	1.35***	e _{aq} ⁻ and/or H ⁺
Furosemide	-0.314*	0.981***	Other radicals
Antipyrine	-0.384***	0.452***	Other radicals
Gemfibrozil	0.660	2.18***	Other radicals

concentrations decrease progressively through the light pathway due to

their short lifetime and limited diffusion rates [33]. The degradation rate of an OMP depends on its susceptibility towards VUV/UV photons, reactivity towards the radicals generated in the water matrix, and the radical concentrations in the reaction layers. With a specific TBA concentration, the contributions of three degradation pathways were determined based on their respective degradation rate constants (Table 1). The potential contribution of secondary radicals to VUV photolysis was estimated using the c/b ratio (Table 2). Under low TBA concentration, HO[•] concentration was high, leading to high overall OMPs degradation, with HO[•]-induced radical-induced degradation being the primary pathway for the abatement of most OMPs (Fig. 3). After 4.5 min of VUV/UV irradiation (total absorbed energy of 35,715 J m⁻³), nineteen OMPs achieved over 90% removal, with radical-induced degradation being the dominant pathway for eighteen OMPs. Atrazine showed relatively low removal because of its low reaction rate constant with HO[•] [34]. In contrast, ketoprofen degraded rapidly because of its high sensitivity to UV_{253.7nm} photons (Table S2.1), resulting in around 80% contribution from UV photolysis to the overall degradation [35]. Similarly, UV photolysis played a significant role in the degradation of diclofenac and sulfamethoxazole, accounting for over 20% of their total abatement. Meanwhile, the contributions of VUV photolysis to the overall degradation of these compounds were 9% and 3%, respectively. Among UV-persistent compounds, some exhibited reactivity towards VUV photons, for example, approximately 6% of ibuprofen and paracetamol degradation were attributed to VUV photolysis. Notably, 1H-benzotriazole exhibited significant VUV photolysis, contributing 32% to its overall degradation. Moreover, secondary radicals, e.g., O₂⁻ and HO₂⁻, could contribute to their degradation as discussed in section 3.3 (red hatched area in Fig. 3). In contrast, some compounds, e.g., propranolol, DEET, and carbamazepine, demonstrated high resistance to

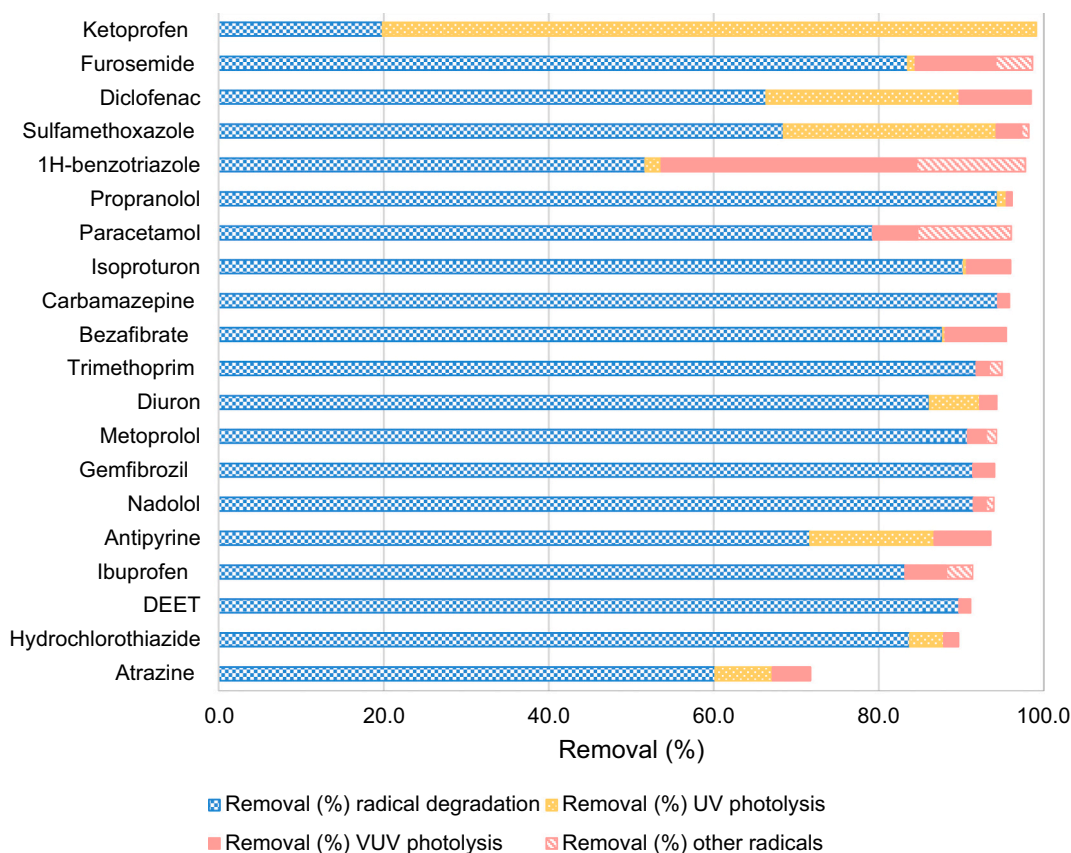


Fig. 3. Degradation of twenty OMPs under a scavenging condition equivalent to 0.06 mmol L⁻¹ TBA, and the contributions of three degradation pathways were determined. The red hatched area represented the possible overestimation of direct VUV photolysis by secondary radical-induced degradation, estimated based on the data reported in Table 2. Treatment time 4.5 min, total absorbed energy 35,715 J m⁻³, absorbed VUV energy 32,400 J m⁻³, pH 5.6, initial concentration 0.06 μmol L⁻¹ for each OMP. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

both UV and VUV radiation.

In the scenario of high scavenging conditions, the availability of $\text{HO}^\bullet$ for OMPs degradation was significantly reduced, leading to a notable decrease in overall removal (Fig. 4). In a scavenging condition equivalent to 1.01 mmol L^{-1} TBA, only the removal of ketoprofen, 1H-benzotriazole, and diclofenac exceeded 90% removal after 4.5 min of treatment. However, the importance of direct photolysis became evident. The total direct photolysis emerged as the predominant degradation pathway for thirteen OMPs, surpassing the contribution of $\text{HO}^\bullet$ radical-induced degradation. For instance, the contribution of VUV photolysis to the degradation of diclofenac and sulfamethoxazole more than doubled compared to the low scavenging scenario, while radical-induced degradation was effectively suppressed. Combined with UV photolysis, total photolysis was estimated to be over 70% of diclofenac and sulfamethoxazole abatement. Additionally, VUV photolysis became the substantial degradation pathway for ibuprofen (37%), bezafibrate (56%), paracetamol (25%), furosemide (48%), antipyrine (26%), and 1H-benzotriazole (63%), indicating their affinity towards VUV photons. A similar susceptibility to VUV photolysis under high $\text{HO}^\bullet$ scavenger conditions was observed for 1H-benzotriazole, bezafibrate, carbamazepine, and atrazine, where the quantum yields of 1H-benzotriazole and bezafibrate were reported to be higher at 184.9 nm than at 253.7 nm [13]. Notably, OMPs degradation via secondary radicals—formed during the VUV water photolysis—can be mistakenly attributed to VUV photolysis if not properly accounted for. For example, while VUV photolysis contributed more than 63% of 1H-benzotriazole removal, approximately 27% of its degradation could be attributed to reactions with $\text{O}_2^{\bullet-}$ or other secondary radicals (red hatched area in Fig. 4). Overestimation of VUV photolysis could also occur in sulfamethoxazole, paracetamol, and furosemide (red hatched area in Fig. 4). Even

compounds such as carbamazepine, which are not typically sensitive to VUV irradiation, exhibited measurable VUV photolysis under high scavenger concentrations. Degradation of carbamazepine via $\text{O}_2^{\bullet-}$ was not observed in this study, despite previous studies suggesting a correlation [36]. For the majority of compounds in this study, VUV photolysis proved to be an important degradation pathway, particularly under high scavenging conditions. The scavenging conditions of a water matrix substantially influence contaminant degradation rates and pathways, making it a crucial consideration when comparing contaminant treatability across different water matrices. To better assess the sensitivity of OMPs to VUV photons, molar extinction coefficients and quantum yields at 184.9 nm could serve as valuable indicators, similar to the categorization of OMPs in this study. However, such photochemical data remains unavailable for many common OMPs, highlighting a critical gap in current knowledge.

4.2. Limitations of the method

Direct photolysis at 184.9 nm during VUV/UV processes is an important yet often overlooked degradation pathway for OMPs removal. In this study, the contributions of VUV photolysis, UV photolysis, and radical-induced degradation to OMPs removal were assessed. Additionally, the impact of secondary radicals generated through VUV water photolysis was evaluated, as their effects could be considered part of the VUV photolysis contribution, by removing DO from water and adding CHCl_3 as a scavenger. However, maintaining stable and extremely low DO concentrations by purging N_2 gas into water prior to treatment proved challenging. Despite best efforts, complete elimination of DO was not achieved, and DO levels fluctuated, resulting in the formation of low levels of $\text{O}_2^{\bullet-}$ and $\text{HO}_2^\bullet$ and increased uncertainty in replicate

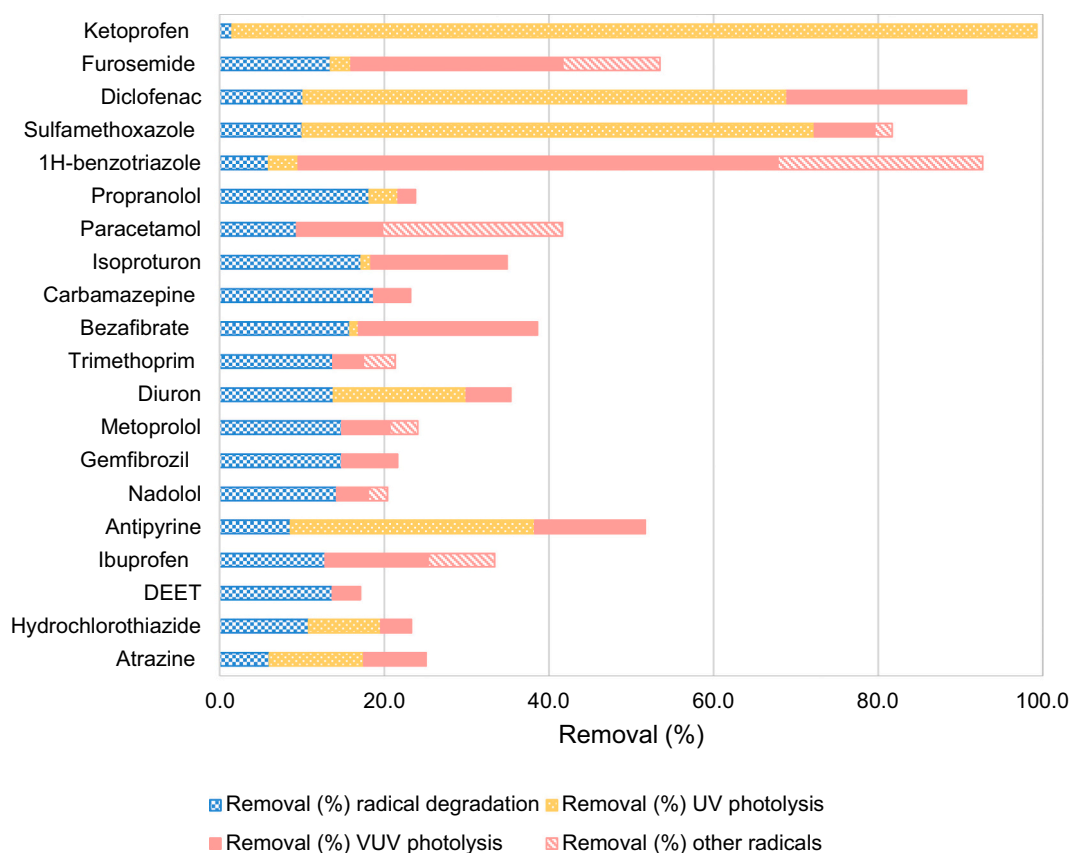


Fig. 4. Degradation of twenty OMPs under a scavenging condition equivalent to 1.01 mmol L^{-1} TBA, and the contributions of three degradation pathways were determined. The red hatched area represented the possible overestimation of direct VUV photolysis by secondary radical-induced degradation, estimated based on the data reported in Table 2. Treatment time 4.5 min, total absorbed energy $35,715 \text{ J m}^{-3}$, absorbed VUV energy $32,400 \text{ J m}^{-3}$, pH 5.6, initial concentration $0.06 \text{ } \mu\text{mol L}^{-1}$ for each OMP. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

experiments (green triangle symbols in Fig. 2). Although CHCl_3 could effectively scavenge $\text{O}_2^{\cdot-}$, its own photolysis and reactions with e_{aq}^- may produce other radicals [31], potentially introducing inaccuracies when evaluating VUV photolysis contributions.

Furthermore, reactive species formed during the degradation of OMPs and TBA likely increased the uncertainty in assessing VUV photolysis, complicating the precise determination of its role. A cocktail solution containing twenty OMPs was used to represent a broad range of contaminants, which may introduce additional uncertainties, as transformation products could potentially scavenge radicals or absorb photons and thereby influence the degradation of other compounds. However, given the low initial concentration of each OMP, such product-mediated interference is expected to be limited. While conducting single-compound degradation studies might reduce the influence of secondary radicals formed during the reactions of co-existing compounds, this approach is less efficient and sustainable from an experimental perspective. In reality, eliminating interference from all radicals is nearly impossible, as radicals can be generated from matrix constituents and OMP transformation reactions during VUV/UV processes. Instead, determining the fundamental photochemical characteristics, particularly at 184.9 nm, and incorporating these into kinetic modeling studies would provide a more practical and effective approach for future research on OMP degradation and the advancement of VUV/UV technologies.

This study was conducted using a lab-scale collimated beam, which may not fully reflect the conditions encountered in scaled-up systems. However, a mechanistic study with a collimated beam provides a controlled framework to isolate and assess individual degradation pathways during VUV/UV processes, offering insights for future reactor design, for example by enabling more effective utilization of direct photolysis to treat OMPs that are resistant to $\text{HO}^{\cdot}$ -induced oxidation. Effective mixing is essential to ensure an even distribution of OMPs across water layers and to facilitate OMPs diffusion to the illuminated volume. In this study, a collimated beam setup with constant magnetic stirring provided adequate mixing for each degradation experiment. Nevertheless, achieving uniform mixing in scaled-up systems is often more challenging. Thus, the contribution of direct photolysis to OMP degradation may vary according to reactor design. Furthermore, the reactor path length should be optimized for the efficient utilization of both UV and VUV light. Long path lengths favor UV light due to its high penetration, providing a larger UV-illuminated volume. Conversely, short path lengths with effective mixing benefit VUV radiation absorption, but the efficiency of UV light may not be fully exploited.

The $\text{HO}^{\cdot}$ scavenger used in this study, TBA, functions as an idealized scavenger by exhibiting negligible UV and limited VUV photon absorption (Table S2.2) and low reactivity with reductive radicals such as e_{aq}^- and $\text{H}^{\cdot}$, making it well suited for isolating direct photolysis during VUV/UV processes. Notably, TBA does not fully represent the complex organic composition of real water, where multiple organic constituents can react with radicals and generate secondary radicals simultaneously. Moreover, the various organics present may have different absorption properties for UV and VUV photons, leading to variable shielding effects that influence degradation. Nevertheless, the use of TBA remains essential for controlled pathway-level assessment during VUV/UV processes, while complementary experiments using real water matrices are equally important for evaluating process performance under environmentally relevant conditions.

4.3. Implication for real water

To further examine VUV processes under realistic conditions, canal water and tap water were spiked with 20 OMPs and treated under VUV/UV and UV irradiation, respectively. Canal water contained 17.6 mg L^{-1} dissolved organic carbon (DOC) and negligible levels of anions, whereas tap water was characterized by relatively high anion concentrations, especially $1.2 \text{ mmol L}^{-1} \text{Cl}^-$, but a lower DOC level of 2.9 mg L^{-1}

(Table S2.4). Both DOC and Cl^- exhibit high absorption coefficients at 184.9 nm [37], resulting in VUV absorbances of 9.6 cm^{-1} for canal water and 7.0 cm^{-1} for tap water (Table S2.4). Canal water and tap water showed 0.37 cm^{-1} and 0.02 cm^{-1} absorbance at 253.7 nm , respectively. Compared with milli-Q water, where VUV absorption is dominated by water molecules, DOC in canal water and anions in tap water substantially reduced the effective VUV fluence available for water photolysis and direct OMP photolysis. Approximately 57% of VUV photons were absorbed by DOC in canal water, while 61% and 12% were absorbed by Cl^- and NO_3^- in tap water, respectively. In addition, DOC is a strong $\text{HO}^{\cdot}$ scavenger, with reaction rate constants on the order of $10^8 \text{ L mol}^{-1} \text{ s}^{-1}$, indicating a high scavenging capacity [38]. All OMPs showed significant degradation in both water matrices, with better performance in tap water (energy-based degradation kinetics shown in Fig. S3.4). For UV sensitive compounds, e.g., ketoprofen, diclofenac and sulfamethoxazole, UV photolysis remained the dominant removal pathway (Fig. S3.3), and matrix effects were limited. For UV-resistant compounds, VUV-induced radical-induced degradation and/or VUV photolysis were the main contributors (Fig. S3.4). In tap water, most VUV photons were absorbed by Cl^- and inorganic carbons, leading to the formation of additional reactive species, e.g., $\text{Cl}^{\cdot}$, that could contribute to OMP degradation. By contrast, in canal water the majority of VUV photons were absorbed by DOC [37], and combined with its strong radical scavenging capacity, this resulted in lower degradation rates compared to tap water and milli-Q (Fig. S3.4). Nevertheless, significant OMP degradation was still observed in canal water, demonstrating the potential of VUV processes for treating waters with high DOC content.

Recognizing the impacts of DOC and anions is essential, especially when considering tailored pre-treatment strategies for VUV-based water treatment. In most natural waters such as surface water, DOC levels vary from 2 to 20 mg L^{-1} , leading primarily to radical scavenging and thereby enhancing the relative importance of direct photolysis in OMP degradation during VUV processes. Under low scavenging conditions as discussed in section 4.1 (0.05 mmol L^{-1} TBA), VUV photolysis could still be an important pathway for OMPs removal. Given the significance of direct photolysis even at lower DOC levels, reactor scaling-up and process optimization could strategically leverage this degradation pathway. Recommendations include enhancing mixing within the reactor, improving illuminated areas, and implementing targeted pre-treatments tailored to specific water types that increase VUV fluence delivered per electrical energy expended.

5. Conclusion

This study evaluated the relative contributions of radical-induced degradation, UV photolysis, and VUV photolysis to the abatement of twenty OMPs during VUV/UV treatment. By systematically controlling radical-induced degradation through the addition of various concentrations of TBA and by distinguishing between VUV/UV and UV-only illumination, the individual contribution of VUV photolysis was explicitly assessed. The results demonstrated that VUV photolysis can be a significant degradation pathway, especially under conditions of strong radical scavenging by the matrix. Even when radical-induced degradation was dominant, for some OMPs VUV photolysis still accounted for a substantial fraction of overall removal. Experiments conducted with tap water and canal water further showed that, despite strong photon competition and radical scavenging from inorganic anions and DOC, significant OMP removal was achieved, highlighting the potential of VUV-based processes in realistic matrices. Inorganic anions, particularly chloride, as well as DOC, strongly absorb VUV photons and generate alternative reactive species, which can complicate the assessment of direct VUV contributions. Overall, this study demonstrates that direct VUV photolysis is not a negligible side process but an important pathway in OMP degradation. Its role should be explicitly included in mechanistic investigations, kinetic modeling, and the design of VUV/UV

photoreactors. These findings provides pathway-level mechanistic evidence that can support more accurate process modeling and guide the advancement of VUV/UV technologies for OMP abatement in water treatment.

CRediT authorship contribution statement

Yicheng Wang: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Bas A. Wols:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Tomas Lock Feixas:** Writing – review & editing, Methodology, Formal analysis. **Wolfgang Gernjak:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2026.110450>.

Data availability

Data will be made available on request.

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