

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: http://www.elsevier.com/locate/jenvman



UV filters as a driver of the antibiotic pollution in different water matrices



Ivana Grgić^{a,1}, Ana-Marija Čižmek^{b,1}, Sandra Babić^b, Davor Ljubas^c, Marko Rožman^{a,*}

^a Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia

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

^c Department of Energy, Power Engineering and Environment, Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, 10000 Zagreb, Croatia

ARTICLE INFO

Keywords: Photodegradation Benzophenone Ethylhexyl methoxycinnamate Advanced wastewater treatment Environmental fate Toxicity driver

ABSTRACT

Antibiotic pollution is frequently detected in fresh waters and wastewaters where they represent an environmental risk for the development of global antibiotic resistance. Due to their excessive use in personal care products, UV filters have also been found to be pseudo-persistent in the aquatic environment. In contrast to antibiotics, which can undergo photodegradation, UV filters are compounds designed to stably absorb UV radiation. This study explored the light based remediation of representative antibiotics from seven classes of antibiotics (fluoroquinolones, tetracyclines, penicillins, macrolide, glycolpeptide, sulphonamides and trimethoprim) in order to assess whether antibiotic pollution persists longer in the presence of organic UV filters. We show that the presence of UV filters either completely supresses or significantly alters the photodegradation of antibiotics in water. Advanced technologies in wastewater treatment, such as the use of UV C radiation, both effectively minimise the effect of UV filters and degrade most of the tested antibiotics proving to be effective management strategy. However, the half-life of erythromycin and amoxicillin, widely used antibiotics from macrolide- and penicillin-like classes, is extended in the presence of UV filters, even during UV C irradiation. Overall, the UV filters present within environmental mixtures are identified as important drivers of mixture toxicity, as they prolong antibiotic contamination of aquatic and engineered environments. The ramification of such finding is that inadequate consideration of UV filters may result in an imperfect prediction of the solar and UV light-based remediation of antibiotics, lead to improper classification of antibiotics persistence in the environment and cause non-optimal chemical fate and transport model performance. Use of the more benign compounds and assessment of the UV filters were identified as feasible management options in minimizing the influence of UV filters onto the remediation of antibiotics in aquatic environments.

1. Introduction

Antibiotics are widely used antimicrobial pharmaceuticals and, as such, result in a continuous input into the environment (Carvalho and Santos, 2016; Kümmerer, 2009a). Water pollution caused by antibiotics receives much attention due to the severe adverse impacts it has on the environment. Antibiotics have been found to cause the modification of microbial community composition and induce the formation of antibiotic-resistant genes (Wang et al., 2020). Moreover, they can bioaccumulate at both lower and higher trophic levels and can enter terrestrial ecosystems due to food web coupling (Previšić et al. submitted for publication). In addition to sorption and biodegradation, photodegradation is one of the main removal processes in surface waters and may be a primary factor in determining the environmental fate of antibiotics (Boreen et al., 2003). For example, broad-spectrum antibiotics, such as fluoroquinolones, tetracyclines and sulphonamides, have been found to undergo direct and indirect photolysis in surface waters and wastewater effluents (Challis et al., 2014; Kümmerer, 2009a). Lower photodegradation rates with a half-life within the range of one to several days were detected for the penicillin/ β -lactam antibiotic amoxicillin, the macrolide antibiotics roxithromycin and erythromycin, the glycolpeptide antibiotic vancomycin and the sulfamethoxazole synergist trimethoprim (Batchu et al., 2014; Lofrano et al., 2014; Ryan et al., 2011; Xu et al., 2011). Accordingly, it has been suggested that allowing photolysis in wastewater stabilization ponds or wastewater treatment wetlands may lead to the enhanced removal of antibiotics prior to discharge (Ryan et al., 2011). Moreover, advanced wastewater treatments such as UV photolysis, UV/H₂O₂ advanced oxidation (Keen and

* Corresponding author.

https://doi.org/10.1016/j.jenvman.2021.112389

Received 7 January 2021; Received in revised form 9 February 2021; Accepted 3 March 2021 Available online 31 March 2021 0301-4797/ $\[mathbb{C}\]$ 2021 Elsevier Ltd. All rights reserved.

E-mail address: marko.rozman@irb.hr (M. Rožman).

¹ These authors contributed equally to this work.

Linden, 2013), TiO_2 assisted photocatalytic oxidation and other advanced oxidative treatment (Kurt et al., 2017) have been revealed as promising management strategies for the efficient removal of antibiotics.

Due to an increased awareness of the negative effects of UV radiation on organisms, the production and use of protective UV filters has increased over the past few decades. As a consequence of their widespread use, UV filters have been detected in recreational waters, freshwaters, sewage, sludge, sediments and soil, and have become a significant constituent of the "chemical pollutant mixture" (Cuderman and Heath, 2007; Ramos et al, 2015, 2016). Similarly for antibiotics, conventional wastewater treatment plants are unable to remove or degrade them (Ramos et al, 2015, 2016). In contrast to antibiotics, which have been found to undergo direct and indirect photodegradation, UV filters are compounds designed to absorb UV radiation and are characterized by high photostability. Presence of UV filters in environmental mixtures could prolong antibiotics persistence in the environment, property of particular importance in the assessment of the environmental significance of substances. Moreover, UV filters could affect the efficiency of wastewater treatment based on photochemical processes, one of the first management strategies for the reduction of the input of pharmaceuticals into the environment (Kümmerer, 2009b). Therefore, understanding antibiotics-UV filters interaction is needed for the correct prediction of photodegradation properties of antibiotics in surface water environments, as well as in engineered conditions. There is very limited research reporting the effects of UV filters on the photodegradation of organic pollutants in water matrices. To our knowledge, there is only one report that demonstrates reduced UV254 nm photolysis of benzotriazole in the presence of the UV filter benzophenone-3 (Liu et al., 2011).

To investigate whether antibiotic pollution will persist longer in the aquatic environment in the presence of UV filters, we explored the photolytic degradation of representative antibiotics from seven classes of antibiotics (fluoroquinolones, tetracyclines, penicillins, macrolide, glycolpeptide, sulphonamides and trimethoprim) in a mixture with the most common UV filters found in aquatic environments. The photo-degradation of antibiotics was explored in three different matrices (ultra-pure water, spring water and wastewater) under the influence of artificial solar and UV C radiation.

2. Experimental section

2.1. Materials

The antibiotics (enrofloxacin, erythromycin, trimethoprim, oxytetracycline, sulfamethoxazole, vancomycin and amoxicillin) and UV filters (benzophenone-3 (BP-3), benzophenone-4 (BP-4) and ethylhexyl methoxycinnamate (EHMC)) used in this study were obtained from Sigma-Aldrich (Taufkirchen, Germany). Sulfametazine and febantel (Veterina Animal Health, Kalinovica, Croatia) were used as internal standards for quantification. HPLC grade solvents and modifiers were purchased from Fisher Scientific (UK).

2.2. Aqueous matrices

The photolysis of antibiotics was studied within three aqueous matrices: ultra-pure, spring and synthetic wastewater. Ultra-pure water (pH = 6.98, conductivity 35.09 μ S/cm) was prepared using a Millipore Simplicity UV system (Millipore Corporation, Billerica, MA, USA). Spring water (pH = 6.87, conductivity 35.09 μ S/cm, Cl⁻ 1.7 mg/L, SO₄²⁻ 1.9 mg/L, NO³⁻ 7.8 mg/L, TOC (total organic carbon) 0.2662 mg/L) was collected from the spring Vrelo in Fužine, Croatia. Spring water samples were filtered using a 0.45 μ m membrane fibre filter to remove any particles and microorganisms, then stored in the dark at 4 °C until the experimental solutions were prepared. The synthetic wastewater was prepared according to (Babić et al., 2013) in order to resemble the

composition of wastewater effluent from pharmaceutical industries. Briefly, 1000 mg/L NaCl, 50 mg/L of citric acid, 30 mg/L of ascorbic acid, 100 mg/L of saccharose and 230 mg/L Na₂HPO₄ was dissolved in a tap water. The pH value for synthetic wastewater was 6,10.

2.3. Photodegradation experiments

The photolysis experiments were conducted in a:

- a) Suntest CPS + simulator (Atlas, Germany) equipped with a Xenon lamp and temperature sensor. The device emitted radiation in the wavelength range of 300–800 nm to simulate natural sunlight. During the experiments the radiation intensity was maintained at 250 W/m^2 and the reaction temperature was kept at (25 \pm 2)°C.
- b) UV C reactor that consisted of a 110 mL borosilicate glass cylinder (200 mm in height and 30 mm in diameter) with a lamp placed in the middle of the cylinder. The lamp was mercury low-pressure lamp, model Pen-Ray 90-0004-07, with $\lambda_{max} = 185/254$ nm, manufactured by UVP (Upland, CA, USA). A scheme of the reactor set-up was published elsewhere (Ćurković et al., 2014).

For the photodegradation experiments, the water matrices were spiked with antibiotic mixture. The initial concentration of each antibiotic in a mixture was 300 μ g/L with exception of vancomycin which was added at a concentration of 500 μ g/L. In the experiments with UV filters, the mixture of all three UV filters was added, each at a concentration of 300 μ g/L. The photodegradation reaction was initiated by exposing the reaction mixture to simulated natural sunlight or UV C light. Irradiation time varied from up to 300 min for simulated solar light to up to 120 min for UV C light. During irradiation time 11 samples were taken at logarithmic scale (i.e. more frequent sampling at the beginning of the experiment) ensuring to obtain at least five data points in the degradation curve. Control samples were collected in all experiments. We ensured that the controls were identical in composition and kept under the same conditions but were protected from light exposure. All experiments were performed in triplicate.

2.4. Analytical determination

Concentrations of the target compounds were determined by an AmaZon ETD mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) coupled with an Ultimate 3000 RSLCnano UHPLC (Dionex, Amsterdam, The Netherlands). The sample injection, separation, and MSMS acquisition was carried out automatically. The samples were loaded (injection volume of 20 µL) onto the Acquity UPLC HSS T3, 50 mm \times 2.1 mm (Waters, Wexford, Ireland) column without any pretreatment. The solvents used for UPLC separation were methanol (solvent A) and 20 mM ammonium formate at a pH of 4 (solvent B). The mixtures of all antibiotics, except vancomycin, were separated using the following 11 min gradient: initial conditions 30% A; 0.0-0.5 min, 30% A; 0.5-7.0 min, 30%-95% A; 7.0-9.0 min, 95% A; 9.0 min, 30% A; 9.0-11.0 min, 30% A. Gradient used for vancomycin was following: initial conditions 10% A; 0.0-6.0 min, 10%-50% A; 6.0-8.0 min, 50%-80% A; 8.0 min, 10% A; 8.0-9.0 min, 10% A. The mass spectrometer operated under unit resolution in selected reaction monitoring (SRM) mode. Positive ionisation mode was used and the electrospray capillary voltage was set at -4500 V. The temperature and flow rate of the drying gas were set at 200 °C and 5 L/min, respectively. Helium was used as the collision gas. The following quantifier transitions were monitored in SRM mode: I) amoxicillin 366.1 > 348.7 m/z at the retention time 1.2 min (isolation with 3 m/z, fragmentation amplitude 0.3 V), II) enrofloxacin 360.2 > 315.9 m/z at the retention time 4.5 min (isolation with 3 m/z, fragmentation amplitude 0.7 V), III) erythromycin 734.5 > 576.3 m/z at the retention time 7 min (isolation with 3 m/z, fragmentation amplitude 0.7 V), IV) oxytetracycline 461.2 > 449.7 m/z at the retention time 3.6 min (isolation with 3 m/z, fragmentation amplitude 0.3 V), V)

sulfamethoxazole 254.1 > 156.5 m/z at the retention time 2.9 min (isolation with 3 m/z, fragmentation amplitude 0.7 V), VI) trimethoprim 291.1 > 229.7 m/z at the retention time 2.2 min (isolation with 3 m/z, fragmentation amplitude 0.7 V), VII) vancomycin 724.7 > 1305.4 m/z at the retention time 4.6 min (isolation with 3 m/z, fragmentation amplitude 0.25 V). To confirm the identity of the parent compound, the entire tandem MS spectrum was considered. Compounds were quantified using QuantAnalysis (Bruker Daltonik GmbH, Bremen, Germany) and Bquant tool (Rožman et al., 2018; Rožman and Petrović, 2016). Matrix-matched calibration curves were constructed, and limits of quantification (LOQ) were defined as the lowest point of the calibration curve with a signal-to-noise (S/N) ratio \geq 10.

2.5. Data analysis

Photodegradation of the target compound is assumed to follow firstorder kinetics. The first-order rate constants were determined by using non-linear regression to fit data and linear regression to fit lntransformed data. Student's t-test was conducted to compare rate constants of different treatments with their respective controls. Rate constants were reported if the treatment was significantly different from control. Reported values are represented as mean \pm standard error. The impact of UV filters, water matrices and their interactions was analysed by two-way ANOVA. Simulated solar light data did not satisfy the assumptions of ANOVA even upon transformations (log- and square root). We therefore employed a robust factorial ANOVA with the corresponding post-hoc test. Statistical significance was set at p < 0.05. Determination of rate constants and statistical evaluation were conducted in Microsoft Excel (2010 Microsoft Corporation) and RStudio 1.2.1335 (RStudio Team (2020). RStudio: Integrated Development for R. RStudio, PBC, Boston, MA, USA).

2.6. Electric energy consumption

Electric energy consumption for UV C radiation experiment was measured by using the VOLTCRAFT energy meter (model Energy Check 3000).

3. Results

3.1. Photodegradation of antibiotics under simulated solar light

Photodegradation was detected for all studied antibiotics except for trimethoprim, Fig. 1. The antibiotics exhibited varying photodegradation trends in respect to the effect of aqueous matrices (ultrapure water, freshwater and wastewater) and the presence of UV filters, Fig. 1.

3.1.1. Effect of UV filters

Addition of the UV filters lowered photodegradation rates of enrofloxacin, oxytetracycline, sulfamethoxazole and vancomycin by, on average, 39.4%, thus equally extending their half-life, Fig. 1. Furthermore, photolysis of amoxicillin and erythromycin ceased completely. A significant main effect of the UV filters on the photodegradation of all antibiotics (except for trimetoprim) was detected, Table S1 - Supplementary material.

3.1.2. Water matrix effect

There was a significant main effect of the water matrices on the photodegradation rate of enrofloxacin, oxytetracycline, vancomycin, sulfamethoxazole and erythromycin, Table S1 - Supplementary material. Enrofloxacin, oxytetracycline and vancomycin showed an increase in photodegradation rate as the complexity of the water matrix rose, Fig. 1. Within this group, two different patterns were observed. Enrofoxacin and oxytetracycline exhibited significant variation of photodegradation rate of vancomycin significantly differed only between the wastewater and ultrapure water. In contrast to the first group, sulfamethoxazole and erythromycin showed a decrease in photodegradation rate with an increase in water matrix complexity, Fig. 1. For amoxicillin no change in photodegradation kinetics with respect to the water matrix was detected, Fig. 1.

3.1.3. Interaction effect between water matrices and UV filters

No significant interaction effect between aqueous matrices and the presence/absence of UV filters on photodegradation rates was observed for any of the studied antibiotics.



Fig. 1. Simulated solar light photodegradation rate constants for the antibiotics used in the experiment. Rate constants (mean \pm standard error) are depicted for various aqueous matrices (ultrapure water, freshwater and wastewater), both with and without the presence of UV filters. Accompanying values can be found in Table S3 – Supplementary material.

3.2. Photodegradation of antibiotics under UV C irradiation

All studied antibiotics were found to be photodegradable under UV C irradiation. The average half-life of antibiotics in wastewater was 0.0815 \pm 0.015 min, while in the wastewater with UV filters, the average half-life was 0.0739 \pm 0.013 min. The change in a light source from the Suntest simulator to the UV C lamp increased photodegradation rates of amoxicillin, erythromycin, sulfamethoxazole and vancomycin, Fig. 2. Moreover, photodegradation was detected for trimethoprim under UV C light, in contrast to simulated solar light where no decay was observed. For enrofloxacin and oxytetracycline, the difference in reaction rates with respect to the light source was not significant.

3.2.1. Effect of the UV filters

Photodegradation rates of the antibiotics in wastewater solution with UV filters did not differ significantly from the solution without UV filters, except for erythromycin, Fig. 2 and Table S2 - Supplementary material. In the case of erythromycin the addition of UV filters significantly lowered reaction rates by 74%, t(4) = 7.81, p < 0.05.

3.2.2. Electric energy consumption

- a) Suntest CPS + simulator The electric energy required for this experiment was irrelevant, because the intention of the authors was to show exposure of the experimental solution to the natural solar radiation, in which case there would be no energy consumption.
- b) UV C reactor The average necessary electric power for the experimental set-up was 21.8 W for reactor with 0.11 L of water solution (corresponds to specific electric power of 198.19 W/L or 198.19 kW/m³). The devices that consumed electric energy in the experiment were the UV C lamp and a magnetic stirrer. The energy for keeping the thermostatic conditions was not included in the calculation.

4. Discussion

Photolysis is one of the main processes for the removal and/or attenuation of antibiotics from wastewater treatment plants (WWTPs) and aquatic environments. Our results demonstrate that the presence of UV filters either completely suppresses the photodegradation of certain antibiotics or significantly alter the photodegradation vield, thus extending the half-life of antibiotics in aquatic environments by a dramatic 40%. This is a serious consequence of the use of UV filters, as it extends the persistence of antibiotic contaminants in aquatic environments. Prolonged antibiotic contamination puts additional pressure on primary producers and decomposers, directly altering community composition and indirectly shifting the ecology and biogeochemistry of fluvial ecosystems (Battin et al., 2016; Carvalho and Santos, 2016). In addition, imposed pressure on bacterial populations contributes to the prevalence of antibiotic-resistant bacteria, as well as the occurrence of antibiotic-resistant genes (Carvalho and Santos, 2016). This is especially problematic for quinolone- and macrolide-class antibiotics, as well as for vancomycin glycopeptide antibiotics that are considered a last-line of defence against bacterial infections (Carvalho and Santos, 2016). Extended antibiotic pressure may also lead to unexpected adverse effects in terrestrial ecosystems, since it has been demonstrated that antibiotics from aquatic ecosystems can enter terrestrial food webs due to food web coupling (Previšić et al., 2021. The effects of increased antibiotic contamination will be highest during the summer months, since both antibiotic pressure and the use of UV filters are usually higher during this part of the year (Archundia et al., 2018; Ramos et al., 2015).

The observed effect of the UV filters may have an impact on chemical exposure prediction models at a catchment scale. Usually, laboratory determinations of photolysis rates were used to extrapolate and predict the behavior of photolabile compounds during river transport (Archundia et al., 2018; Lin et al., 2006). Inadequate consideration of water matrix variability due to seasonal variation in the presence of UV filters,



Fig. 2. UV C photodegradation rate constants (mean \pm standard error) of antibiotics in wastewater, with and without the presence of UV filters. Accompanying values can be found in Table S4 – Supplementary material.

among others, may result in an imperfect prediction of the solar light-based remediation of antibiotics, cause non-optimal model performance and lead flawed exposure assessments. Furthermore, our results demonstrate how risk assessments undertaken for single substances and not for mixtures could lead to improper classification of persistence in the environment, particularly important when assessing environmental significance of substances (Kümmerer, 2009b).

The significance and extent of the direct and indirect photolysis of antibiotics in aquatic environments varies for each compound (Kümmerer, 2009a). Our observations are in agreement with previous findings on the effects of water matrices on photodegradation of antibiotics i.e. negative correlation between the degradation rate and the complexity of the water matrix for erythromycin and sulfamethoxazole (Batchu et al., 2014) and the positive correlation between the degradation rate and the complexity of the water matrix exhibited by enrofloxacin, oxytetracycline and vancomycin (Batchu et al., 2014; Jiao et al., 2008; Sturini et al., 2012). It is important to note that water matrices with UV filters follow the same trend regarding photodegradation rates as do water matrices without UV filters. Additional confirmation of this congruency is the lack of interaction between water matrices and UV filters. This is to be expected, as UV filters uniformly adsorb UV radiation and impede direct absorption of a solar photon by both target antibiotics and water present photosensitizers, thus equally lowering the extent of both the direct and indirect photolysis of antibiotics.

The addition of UV filters to water matrices has a great impact on the photodegradation fate of antibiotics, causing their decay reactions to slow down drastically or come to a complete stop. Attenuating this important abiotic degradation path in wastewater matrices, where the highest concentrations of antibiotics are readily detected (Carvalho and Santos, 2016), may be especially problematic. Removal efficiencies of antibiotics in the WWTPs are usually estimated by examining the difference between input and output concentrations (Archundia et al., 2018; Zhang et al., 2020) and a number of assumptions regarding photodegradation rates were applied (Morais et al., 2014). Likewise, for predicating river antibiotic attenuation rates, seasonal variation in the presence of UV filters (among others) may result in imperfect predictions and inadequate modeling of the dynamic fate of antibiotics in the WWTPs, and consequently poor management and control of antibiotic pollution in environment.

Advanced effluent treatment is marked as one of the effective management strategies for the reduction of the environmental impacts of antibiotics and critical node for control of the global spread of antibiotic resistance (Kümmerer, 2009b; Pruden et al., 2013). Using advanced wastewater treatment that includes irradiation of wastewater by the UV C component of the spectrum could lead to a significant improvement in the remediation of antibiotics (Čizmić et al., 2019; He et al., 2014; Yuan et al., 2011). UV C radiation is capable of destroying a large variety of organic pollutants by direct photon absorption and indirect degradation (He et al., 2014). Indeed, our results indicate that the degradation rates of antibiotics were generally much higher under UV C light compared to photodegradation under artificial sunlight. Also, UV C light decreased the impacts of UV filters on the photodegradation rate of most antibiotics. Our analysis illustrates that is highly unlikely that UV filters have any relevant effect on the UV C photodegradation rate of enrofloxacin, trimethoprim, oxytetracycline, sulfamethoxazole and vancomycin. On the other hand, the presence of UV filters in a mixture has shown to increase the half-life of erythromycin by more than 3 times. Moreover, although the difference was not significant for amoxicillin at t(4) = 2.37(p = 0.07), it did represent a large-sized effect of r = 0.76, implying a strong impact on the half-life of amoxicillin. This finding could be explained by the competition for the absorption of UV C radiation by different constituents dissolved in water - mainly UV filters, which is in alignment with the well-known effect of decrease in degradation rates with increased complexity of water matrices (Kümmerer, 2009a). Although this claim needs to be thoroughly tested, a possible implication

may be that UV C irradiation doses used for the mineralisation of antibiotics in wastewaters that do not contain UV filters are insufficient to remove all antibiotics in the presence of UV filters. Therefore, longer exposure times (i.e. larger energy consumption) are required for their removal in advanced wastewater treatment.

The degradation of erythromycin with UV C radiation demonstrates how the presence of UV filters directly raises the overall cost of the treatment. The half-life of erythromycin increased from 241 min without UV filters to 904 min with UV filters, requiring approximately 11 h more UV C irradiation to achieve the same level of erythromycin degradation i.e. electric energy consumption of an additional 2190 kWh per m³ of treated wastewater. Indeed, UV filters may raise the cost of UV based water treatment processes and consequently cause higher emissions of CO_2 , especially when artificial UV light is used, which may be an inhibiting factor for their application in water treatment. However, this problem may be mitigated by the integration of the recently developed semi-conductor light source - UV light-emitting diodes that are more energy efficient (wall plug efficiency up to 75%), have a significantly longer expected lifespan (up to 100.000 working hours) and are more environmental friendly than commonly used mercury lamps (Green et al., 2020; Song et al., 2016). Also, it remains to be seen (beyond the scope of this study) how other advanced wastewater treatment processes perform for removal of antibiotics in the presence of UV filters.

In addition to advanced effluent treatment use of substitution, more benign compounds should be employed as effective environmental management strategy (Kümmerer, 2009b). In this context, design or synthesis of UV filters with negligible or lowest possible influence onto the remediation processes in environmental waters or on the water treatment steps used for antibiotics removal should be encouraged. So far, inorganic physical UV filters such as nano-sized TiO2 might be a suitable alternative. Moreover, TiO2 is used in catalysis and photocatalytic applications for the removal of the antibiotics, although not so effective in rutile form which is used as a UV filter (Menard et al., 2011; Su et al., 2011). However, ecotoxic effects of TiO₂ remain to be established in order to get the complete environmental life cycle assessment (Menard et al., 2011). Meanwhile, a practical strategy for minimizing the effect of UV filters on prolonged antibiotics pollution may include assessing the UV filters by performance tests based on experiments performed in the current study.

5. Conclusion

In this work, we found that the presence of UV filters BP-3, BP-4 and EHMC, commonly found in personal care products, either completely supresses or significantly alters the photodegradation of seven classes of antibiotics. The UV filters present within a mixture become important drivers of mixture toxicity since they prolong antibiotic contamination of aquatic environments, with all of its consequences. Furthermore, our results demonstrate that the assessment of the environmental significance of substances should be undertaken using environmentally resembled multi-component mixtures. We also suggest that the chemical fate and transport models at a catchment scale should test their robustness towards the observed effect of UV filters. Advanced technologies in wastewater treatment, such as the UV C radiation effectively minimises the impact of UV filters and efficiently degrades most of the tested antibiotics. However, the half-life of erythromycin and amoxicillin, widely used antibiotics from macrolide- and penicillin-like classes, is extended in the presence of UV filters, even during UV C irradiation. Thus, UV filters lead to longer operating times and therefore higher electric energy consumption to achieve similar removal of antibiotics. We identified the use of more benign compounds (e.g. inorganic UV filters) and assessment of the UV filters by performance tests based on experiments performed in the study, as management options in minimizing impact of UV filters onto the removal of antibiotics from aqueous matrices.

Credit author statement

Ivana Grgić: Investigation, Methodology, Visualization, Writing original draft. Ana-Marija Čižmek: Investigation, Methodology, Writing - original draft. Sandra Babić: Supervision, Data curation, Writing - review & editing. Davor Ljubas: Investigation, Data curation, Writing review & editing. Marko Rožman: Conceptualization, Funding acquisition, Investigation, Methodology, Data curation, Supervision, Writing original draft, Writing - review & editing.

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.

Acknowledgements

We thank Hasan Muharemović (Ruđer Bošković Institute, Zagreb) and Marko Skozrit (Faculty of Mechanical Engineering and Naval Architecture, Zagreb) for help during laboratory work. Proofreading by Katarina Cetinić (Ruđer Bošković Institute, Zagreb) is gratefully acknowledged. This work was supported by the Croatian Science Foundation project no. IP-2018-01-2298 and the Croatian Academy of Sciences and Arts Foundation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.112389.

References

- Archundia, D., Boithias, L., Duwig, C., Morel, M.C., Flores Aviles, G., Martins, J.M.F., 2018. Environmental fate and ecotoxicological risk of the antibiotic sulfamethoxazole across the Katari catchment (Bolivian Altiplano): application of the GREAT-ER model. Sci. Total Environ. 622 (623), 1046–1055. https://doi.org/ 10.1016/j.scitotenv.2017.12.026.
- Babić, S., Periša, M., Škorić, I., 2013. Photolytic degradation of norfloxacin, enrofloxacin and ciprofloxacin in various aqueous media. Chemosphere 91, 1635–1642. https:// doi.org/10.1016/j.chemosphere.2012.12.072.
- Batchu, S.R., Panditi, V.R., O'Shea, K.E., Gardinali, P.R., 2014. Photodegradation of antibiotics under simulated solar radiation: implications for their environmental fate. Sci. Total Environ. 470–471, 299–310. https://doi.org/10.1016/j. scitotenv.2013.09.057.
- Battin, T.J., Besemer, K., Bengtsson, M.M., Romani, A.M., Packmann, A.I., 2016. The ecology and biogeochemistry of stream biofilms. Nat. Rev. Microbiol. 14, 251–263. https://doi.org/10.1038/nrmicro.2016.15.
- Boreen, A.L., Arnold, W.A., McNeill, K., 2003. Photodegradation of pharmaceuticals in the aquatic environment: a review. Aquat. Sci. 65, 320–341. https://doi.org/ 10.1007/s00027-003-0672-7.
- Carvalho, I.T., Santos, L., 2016. Antibiotics in the aquatic environments: a review of the European scenario. Environ. Int. 94, 736–757. https://doi.org/10.1016/j. envint.2016.06.025.
- Challis, J.K., Hanson, M.L., Friesen, K.J., Wong, C.S., 2014. A critical assessment of the photodegradation of pharmaceuticals in aquatic environments: defining our current understanding and identifying knowledge gaps. Environ. Sci. Process. Impacts 16, 672. https://doi.org/10.1039/c3em00615h.
- Čizmić, M., Ljubas, D., Rožman, M., Ašperger, D., Ćurković, L., Babíc, S., 2019. Photocatalytic degradation of azithromycin by nanostructured TiO 2 film: kinetics, degradation products, and toxicity. Materials 16. https://doi.org/10.3390/ ma12060873.
- Cuderman, P., Heath, E., 2007. Determination of UV filters and antimicrobial agents in environmental water samples. Anal. Bioanal. Chem. 387, 1343–1350. https://doi. org/10.1007/s00216-006-0927-y.
- Ćurković, L., Ljubas, D., Šegota, S., Bačić, I., 2014. Photocatalytic degradation of Lissamine Green B dye by using nanostructured sol-gel TiO2 films. J. Alloys Compd. 604, 309–316. https://doi.org/10.1016/j.jallcom.2014.03.148.
- Green, A., Popović, V., Warriner, K., Koutchma, T., 2020. The efficacy of UVC LEDs and low pressure mercury lamps for the reduction of Escherichia coli O157:H7 and Listeria monocytogenes on produce. Innovat. Food Sci. Emerg. Technol. 64, 102410 https://doi.org/10.1016/j.ifset.2020.102410.

- He, X., Mezyk, S.P., Michael, I., Fatta-Kassinos, D., Dionysiou, D.D., 2014. Degradation kinetics and mechanism of β -lactam antibiotics by the activation of H2O2 and Na2S2O8 under UV-254nm irradiation. J. Hazard Mater. 279, 375–383. https://doi.org/10.1016/j.jhazmat.2014.07.008.
- Jiao, S., Zheng, S., Yin, D., Wang, L., Chen, L., 2008. Aqueous photolysis of tetracycline and toxicity of photolytic products to luminescent bacteria. Chemosphere 73, 377–382. https://doi.org/10.1016/j.chemosphere.2008.05.042.
- Keen, O.S., Linden, K.G., 2013. Degradation of antibiotic activity during UV/H2O2 advanced oxidation and photolysis in wastewater effluent. Environ. Sci. Technol. 47, 13020–13030. https://doi.org/10.1021/es402472x.
- Kümmerer, K., 2009a. Antibiotics in the aquatic environment a review Part I. Chemosphere 75, 417–434. https://doi.org/10.1016/j.chemosphere.2008.11.086.
- Kümmerer, K., 2009b. The presence of pharmaceuticals in the environment due to human use - present knowledge and future challenges. J. Environ. Manag. 90, 2354–2366. https://doi.org/10.1016/j.jenvman.2009.01.023.
- Kurt, A., Mert, B.K., Özengin, N., Sivrioğlu, Ö., Yonar, T., 2017. Treatment of antibiotics in wastewater using advanced oxidation processes (AOPs). In: Physico-Chemical Wastewater Treatment and Resource Recovery, pp. 176–211. https://doi.org/ 10.5772/67538.
- Lin, A.Y.C., Plumlee, M.H., Reinhard, M., 2006. Natural attenuation of pharmaceuticals and alkylphenol polyethoxylate metabolites during river transport: photochemical and biological transformation. Environ. Toxicol. Chem. 25, 1458–1464. https://doi. org/10.1897/05-412R.1.
- Liu, Y.S., Ying, G.G., Shareef, A., Kookana, R.S., 2011. Photostability of the UV filter benzophenone-3 and its effect on the photodegradation of benzotriazole in water. Environ. Chem. 8, 581–588. https://doi.org/10.1071/EN11068.
- Lofrano, G., Carotenuto, M., Uyguner-Demirel, C.S., Vitagliano, A., Siciliano, A., Guida, M., 2014. An integrated chemical and ecotoxicological assessment for the photocatalytic degradation of vancomycin. Environ. Technol. 35, 1234–1242. https://doi.org/10.1080/09593330.2013.865085.
- Menard, A., Drobne, D., Jemec, A., 2011. Ecotoxicity of nanosized TiO2. Review of in vivo data. Environ. Pollut. 159, 677–684. https://doi.org/10.1016/j. envpol.2010.11.027.
- Morais, S.A., Delerue-Matos, C., Gabarrell, X., 2014. An uncertainty and sensitivity analysis applied to the prioritisation of pharmaceuticals as surface water contaminants from wastewater treatment plant direct emissions. Sci. Total Environ. 490, 342–350. https://doi.org/10.1016/j.scitotenv.2014.04.082.
- Previšić, A., Vilenica, M., Vučković, N., Petrović, M., Rožman, M., 2021. Aquatic Insects Transfer Pharmaceuticals and Endocrine Disruptors from Aquatic to Terrestrial Ecosystems. Environ. Sci. Technol. https://doi.org/10.1021/acs.est.0c07609.
- Pruden, A., Joakim Larsson, D.G., Amézquita, A., Collignon, P., Brandt, K.K., Graham, D. W., Lazorchak, J.M., Suzuki, S., Silley, P., Snape, J.R., Topp, E., Zhang, T., Zhu, Y.G., 2013. Management options for reducing the release of antibiotics and antibiotic resistance genes to the environment. Environ. Health Perspect. 121, 878–885. https://doi.org/10.1289/ehp.1206446.
- Ramos, S., Homem, V., Alves, A., Santos, L., 2016. A review of organic UV-filters in wastewater treatment plants. Environ. Int. 86, 24–44. https://doi.org/10.1016/j. envint.2015.10.004.
- Ramos, S., Homem, V., Alves, A., Santos, L., 2015. Advances in analytical methods and occurrence of organic UV-filters in the environment - a review. Sci. Total Environ. 526, 278–311. https://doi.org/10.1016/j.scitotenv.2015.04.055.
- Rožman, M., Acuña, V., Petrović, M., 2018. Effects of chronic pollution and water flow intermittency on stream biofilms biodegradation capacity. Environ. Pollut. 233, 1131–1137. https://doi.org/10.1016/j.envpol.2017.10.019.
- Rožman, M., Petrović, M., 2016. Bquant novel script for batch quantification of LCMS data. MethodsX 3, 520–524. https://doi.org/10.1016/j.mex.2016.09.001.
- Ryan, C.C., Tan, D.T., Arnold, W.A., 2011. Direct and indirect photolysis of sulfamethoxazole and trimethoprim in wastewater treatment plant effluent. Water Res. 45, 1280–1286. https://doi.org/10.1016/j.watres.2010.10.005.
- Song, K., Mohseni, M., Taghipour, F., 2016. Application of ultraviolet light-emitting diodes (UV-LEDs) for water disinfection: a review. Water Res. 94, 341–349. https:// doi.org/10.1016/j.watres.2016.03.003.
- Sturini, M., Speltini, A., Maraschi, F., Profumo, A., Pretali, L., Irastorza, E.A., Fasani, E., Albini, A., 2012. Photolytic and photocatalytic degradation of fluoroquinolones in untreated river water under natural sunlight. Appl. Catal. B Environ. 119–120, 32–39. https://doi.org/10.1016/j.apcatb.2012.02.008.
- Su, R., Bechstein, R., Sø, L., Vang, R.T., Sillassen, M., Esbjörnsson, B., Palmqvist, A., Besenbacher, F., 2011. How the anatase-to-rutile ratio influences the photoreactivity of TiO 2. J. Phys. Chem. C 115, 24287–24292. https://doi.org/10.1021/jp2086768.
- Wang, Z., Han, M., Li, E., Liu, X., Wei, H., Yang, C., Lu, S., Ning, K., 2020. Distribution of antibiotic resistance genes in an agriculturally disturbed lake in China: their links with microbial communities, antibiotics, and water quality. J. Hazard Mater. 393, 122426 https://doi.org/10.1016/j.jhazmat.2020.122426.
- Xu, H., Cooper, W.J., Jung, J., Song, W., 2011. Photosensitized degradation of amoxicillin in natural organic matter isolate solutions. Water Res. 45, 632–638. https://doi.org/10.1016/j.watres.2010.08.024.
- Yuan, F., Hu, C., Hu, X., Wei, D., Chen, Y., Qu, J., 2011. Photodegradation and toxicity changes of antibiotics in UV and UV/H2O2 process. J. Hazard Mater. 185, 1256–1263. https://doi.org/10.1016/j.jhazmat.2010.10.040.
- Zhang, S.X., Zhang, Q.Q., Liu, Y.S., Yan, X.T., Zhang, B., Xing, C., Zhao, J.L., Ying, G.G., 2020. Emission and fate of antibiotics in the Dongjiang River Basin, China: implication for antibiotic resistance risk. Sci. Total Environ. 712, 136518 https:// doi.org/10.1016/j.scitotenv.2020.136518.