


Effect of vacuum UV and UV-C treatment on degradation and ecotoxicity of tire wear microrubber leachates

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ABSTRACT

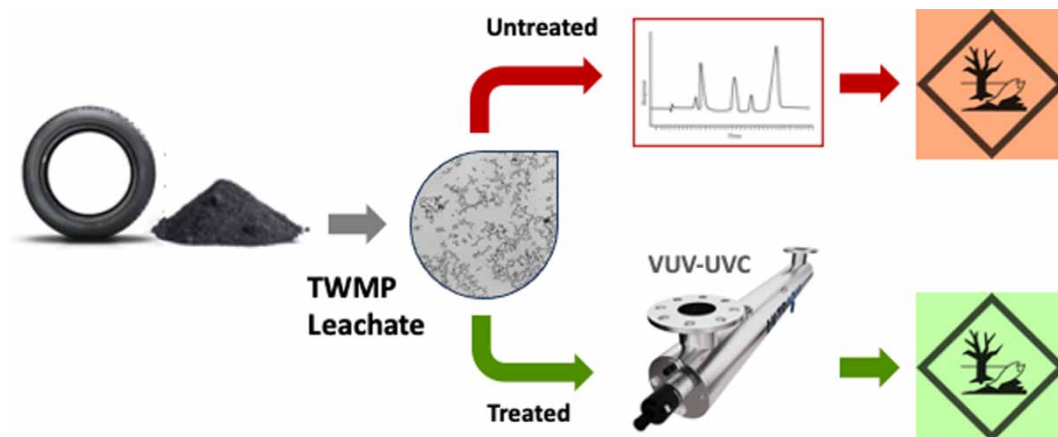
Tire wear microrubber particles (TWMP) are a major source of environmental contamination. Degradation of TWMP is slow and leachates contain toxic constituents including heavy metals, polycyclic aromatic hydrocarbons (PAHs) and organic additives. Few studies have addressed methods to mitigate the potential ecotoxicity of TWMP leachates. This study investigated the effects of UV-C (254 nm) and combined UV-C and vacuum UV (185 nm) treatment (VUV-UV-C) of TWMP leachates on degradation and ecotoxicity. VUV-UV-C treatment mitigated dissolved zinc and degraded the TWMP constituents fluoranthene, pyrene and benzo(a)pyrene by up to 90%, and the additives benzothiazole and phthalates by up to 70%. The potential ecotoxicity and genotoxicity of TWMP constituents were examined before and after UV treatment in bioassays with *Escherichia coli*, the luminescent bacterium *Aliivibrio fischeri*, the microalga *Raphidocelis subcapitata* and the crustacean *Daphnia magna*. VUV-UV-C treatment decreased the potential ecotoxicity up to five-fold as indicated by changes in median effective concentrations (EC50). This was likely due to the formation of less toxic and less bioavailable transformation products. The VUV-UV-C treatment did not require the addition of oxidants or catalysts, and the study indicated a potential of VUV-UV-C as an advanced oxidation process to mitigate toxic compounds in TWMP leachates from urban or industrial sources.

Key words: advanced oxidation processes, ecotoxicity, photochemical degradation, tire rubber, vacuum UV

HIGHLIGHTS

- Leachates from tire wear microrubber particles (TWMP) exhibited a substantial potential for ecotoxicity.
- VUV-UV-C treatment removed toxic compounds from TWMP leachates.
- *In vivo* bioassays showed significantly lower ecotoxicity in VUV-UV-C-treated leachates.
- VUV-UV-C is an effective advanced oxidation technology that does not require the addition of catalysts or oxidant precursors.

GRAPHICAL ABSTRACT



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INTRODUCTION

The largest fraction of microplastic pollution in many countries originates from car tire abrasion resulting in tire wear micro-rubber particles (TWMP) (Boucher & Friot 2017; Kole *et al.* 2017). TWMP are released due to the heat created while driving and the shear forces between the road and the tire. The shear forces result in relatively large particles, while the heat generated on the tire's surface releases smaller particles (Kole *et al.* 2017). TWMP vary in size from less than 2 μm to coarse particles of 500–1,000 μm with average sizes often dominated by smaller particles of less than 100 μm (Grigoratos & Martini 2014; Wagner *et al.* 2018; Gieré & Dietze 2023). The specific TWMP size depends on factors, such as driving speed, driving style, vehicle characteristics, meteorological parameters, tire composition and age and road surface characteristics (Grigoratos & Martini 2014; Kole *et al.* 2017). About 1.3 million tonnes of tire wear are released into the environment each year in Europe (Wagner *et al.* 2018).

Aquatic ecosystems are one of the primary sinks for TWMP and about half of the total microplastic pollution in many aquatic ecosystems stems from tire erosion (Boucher & Friot 2017; Baensch-Baltruschat *et al.* 2020). This large contribution from TWMP to environmental microplastic pollution is not expected to decrease in the near future (Sommer *et al.* 2018). In addition, vehicle tires that are no longer suited for use (end-of-life tires) are occasionally collected and reused to serve different purposes. Such recycled products can also represent significant sources of TWMP pollution. Unfortunately, tire rubber contains a range of potentially toxic substances that can leach into the environment and contaminate soils and surface waters even though the rubber particles themselves are trapped or otherwise immobilized (Wik *et al.* 2009; Wagner *et al.* 2018; Baensch-Baltruschat *et al.* 2020; Capulupo *et al.* 2020; Halle *et al.* 2020; Lu *et al.* 2021; Gieré & Dietze 2023). TWMP toxicants include metals, such as zinc, copper, aluminum, lead, polycyclic aromatic hydrocarbons (PAHs) and additives, such as phthalates, benzothiazoles (BTZ) and N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) (Wagner *et al.* 2018; Gieré & Dietze 2023). It has therefore been suggested that of all possible environmental plastic contaminations, leachates from car tire rubber likely have the greatest toxicological effect on aquatic organisms (Capulupo *et al.* 2020).

Natural degradation of TWMP is slow and can take hundreds or even thousands of years, and some constituents are considered persistent in the environment. Interestingly, UV-based advanced oxidation processes (AOPs) have the potential for the treatment of water containing toxic and persistent substances (Zoschke *et al.* 2014; Duca *et al.* 2017; Lin *et al.* 2020). The underlying principle of UV-based AOPs is the *in situ* generation of radicals such as hydroxyl radicals ($\cdot\text{OH}$) that will react with organic or inorganic constituents in the contaminated water. Vacuum UV (VUV) treatment will generate such radicals including $\cdot\text{OH}$ without the need for additions of catalysts or radical precursors (Zoschke *et al.* 2014). In addition, combined VUV-UVC treatment has the potential for both direct and indirect photolysis of many environmental pollutants. The indirect photolysis is carried out by photochemically produced reactive intermediates generated mainly by VUV (e.g., 185 nm) whereas the direct photolysis is mediated mainly by the UVC radiation (e.g., 254 nm). The latter occurs when the target molecule absorbs light that promotes excitation leading to electron transfer and subsequent degradation. However, it is not known how AOPs such as VUV-UVC affect the ecotoxicity of TWMP leachates, and there is a need to establish basic knowledge regarding changes in toxicity to aquatic organisms before large-scale applications are considered.

This study examined the effects of short-wave UV irradiation on the degradation and ecotoxicity of substances in TWMP leachates. Samples were exposed to different UV regimes including UVC (254 nm) and combined VUV (185 nm) and UVC (VUV-UVC). The kinetics of compound removal was determined in relation to treatment time and UV type and UV fluence (dose). The potential ecotoxicity of TWMP constituents was examined before and after UV treatment using aquatic test organisms to assess treatment efficiency with respect to bioactive compounds and the occurrence of toxic transformation products.

MATERIALS AND METHODS

Tire wear microrubber particles

TWMP were obtained from the tire recycling company Genan (Viborg, Denmark) and consisted of the product GENAN 120 Mesh. This product consists of cryomilled recycled tire rubber with nominal particle sizes $<125 \mu\text{m}$. GENAN 120 is micronized rubber produced from off-road vehicle tires, passenger car tires and truck tires. Genan obtained the size fraction $<125 \mu\text{m}$ by sieving the particles through an Air Jet sieve 200 LS (Hosokawa Alpine). The specific density of the TWMP was 1.16 g/cm^3 . The TWMP were suspended in tap water and the particle size distribution and concentrations of TWMP were determined using a Multisizer™ 4e Coulter Counter (Beckmann-Coulter, USA). Particles were sized and counted using a combination of apertures (50, 100 and 2,000 μm). The tap water used for creating TWMP suspensions consisted of municipal

tap water obtained from Aalborg Municipality (Denmark). The municipality produces tap water from groundwater (12–16 dH) abstracted directly from chalk aquifers without water treatment or disinfection (no chlorination). The nonvolatile organic carbon (NVOC) concentration and the chemical oxygen demand (COD) were 1.3 and 0.4 mg/L, respectively. The pH and turbidity of the tap water were 7.6 and <0.05 FTU, respectively.

This study focused on TWMP leachates rather than rubber particles because less is known about the effects of UV on leachates despite being abundant and somewhat mobile in the environment. TWMP leachates were established by suspending 1 g/L cryomilled tire rubber in tap water in 1 L Bluecap bottles followed by incubating on a magnetic stirrer. The solutions were subsequently transferred to Greiner centrifuge tubes (Sarstedt) and centrifuged at 3,000 g in a ScanSpeed 1236R centrifuge (LaboGene). The supernatants were then filtered through Advantec GF-75 glass fiber filters with a nominal pore size of 0.3 μm (Advantec, Japan) to create TWMP leachates.

VUV and UVC irradiation

Combined VUV and UVC irradiation of aqueous solutions of TWMP leachates and TWMP constituents were carried out using a Collimated UV Beam Tube system (ULTRAAQUA A/S, Denmark) equipped with a 4 W low-pressure high-output amalgam VUV Hg lamp (NIQ 40/18, Heraeus, Germany) (Figure 1). The UV lamp simultaneously emitted VUV (185 nm) and UVC (254 nm) with fluence rates at the collimated beam tube window of 10 and 100 $\mu\text{W}/\text{cm}^2$, respectively. The VUV-UVC Collimated beam system was continuously flushed with N_2 (99.9999%) to limit quenching by O_2 (O_3 formation). The Collimated beam system was temperature controlled at 18 °C using an HTS 15 heat transfer station (Huber). Water samples with TWMP leachates in 25 mL glass petri dishes were placed in direct contact with the Collimated Beam Tube window (no gas phase) to avoid quenching and samples were stirred with a magnetic stirrer during UV irradiation. UV doses (fluence in J/cm^2) were calculated based on measured UVC and VUV irradiance, the water depth and volume in the petri dish, the UV absorption coefficient and the reflection factor (Bolton *et al.* 2015). VUV irradiance was measured using a Hamamatsu H9535-185 VUV Power meter, and UVC irradiance was measured using a ZED Reference UV Radiometer (TinyMeter). To compare the effect of combined VUV-UVC irradiation with the effect of UVC irradiation alone (no VUV), monochromatic UVC irradiation of aqueous solutions of TWMP leachates was carried out using an 8 W UVP 3UV lamp (Analytic Jena) equipped with a monochromatic UVC tube (254 nm). Samples with TWMP leachates in 25 mL glass petri dishes were placed on a magnetic stirrer 12 cm below the UVC lamp. The UVC irradiance was measured using an Extech SDL470 UVC meter and was 120 $\mu\text{W}/\text{cm}^2$ at 12 cm distance.

Experiments for testing the effects of VUV-UVC treatment on large volumes of TWMP leachates were conducted in a continuous-flow UV photoreactor as described previously (Del Puerto *et al.* 2022). The 4 L UV photoreactor (Figure 1) was operated with cooling at 10 °C and a flow of 2 L/min. The UV photoreactor was equipped with a UVC sensor and a low-pressure high-output amalgam VUV Hg lamp which simultaneously emitted VUV (185 nm) and UVC (254 nm) at a radiation

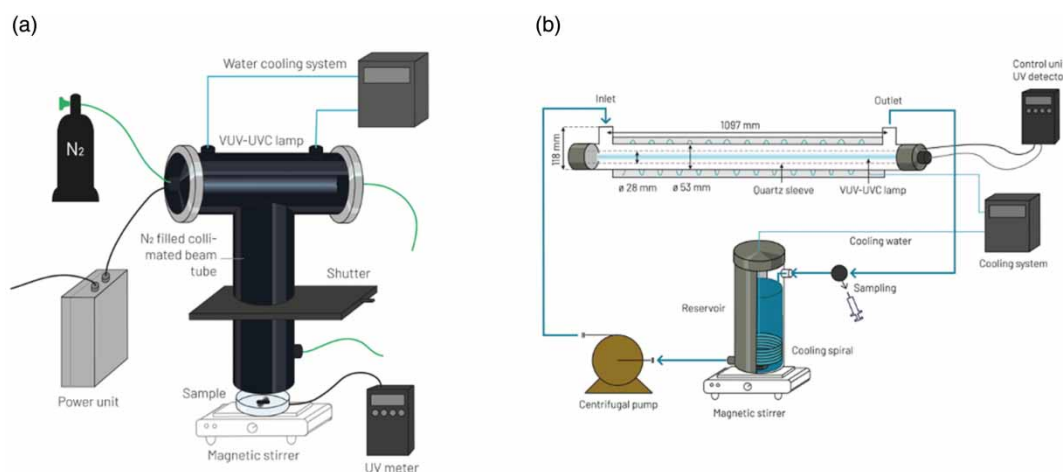


Figure 1 | Collimated beam tube for VUV-UVC irradiation of TWMP leachates (a), and VUV-UVC flow reactor for treatment of large samples of TWMP leachates (b).

flux of 14 and 56 W, respectively (UltraTherm 200 W LPHO TOC UV, Ultraaqua A/S, Denmark). UV fluence (J/cm^2) was calculated on the basis of the measured UV irradiance during the treatments (25–34 mW/cm^2) and the treatment times. The treatment times were varied between 0 and 32 min.

PAHs and organic additives in TWMP leachates

PAHs, BTZ, 6PPD and phthalates in leachates and spiked samples were extracted and quantified partly as described by Polyakova *et al.* (2013). Na_2SO_4 (0.2 g) was added to 2 mL water samples and then extracted with 2 mL toluene-hexane (1:6) followed by centrifugation to separate phases (Polyakova *et al.* 2013). Naphthalene [CAS 91-20-3] and phenanthrene [CAS 85-01-8] were added as internal standards, and the PAH extraction efficiency varied between 83.4 and 101.2%. The toluene-hexane extract was analyzed using an Agilent 7890A Gas Chromatograph equipped with flame ionization detection, a Combi PAL autosampler and a DB5 column (30 m \times 0.32 mm; 0.25 μm film thickness). The initial column temperature was 150 $^\circ\text{C}$ followed by ramping at 15 $^\circ\text{C}/\text{min}$ to 260 $^\circ\text{C}$, and then 6 min at 260 $^\circ\text{C}$. Helium was used as carrier gas. The analysis of PAHs in TWMP leachates focused on phenanthrene, pyrene, fluoranthene and benzo(a)pyrene as model compounds because they are relatively abundant in tire rubber and/or have carcinogenic properties. The analysis of spiked samples before and after UV irradiation included BTZ [CAS 95-16-9], dimethyl phthalate (DMP) [CAS 13-11-3] and diethyl phthalate (DEP) [CAS 84-66-2]. These organics were spiked into water samples at 10 and 100 mg/L without the use of carrier solvents.

Metals in TWMP leachates

The content of metals and other elements in TWMP leachates was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) using an Optima 8,000 system (Perkin Elmer) and inductively coupled plasma mass spectrometry (ICP-MS) using an SCIEX ELAN DRC-e system (PerkinElmer). The following 25 elements were considered: Al, Sb, As, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Ag, Se, Ti, Zn, P, Sr, V, Tl and Ca. Zinc (Zn) was the dominant metal in TWMP leachates and routine measurements of Zn ions were carried out using a Supelco Spectroquant[®] Photometric zinc test (Merck). Zn complexed with a 1-(2-pyridylazo)-2-naphthol derivative was quantified at 565 nm using a Genesys 20 spectrophotometer (Merck).

Ecotoxicity of VUV and UVC-treated TWMP constituents

The ecotoxicity of TWMP leachates and constituents was determined before and after UV treatment. Toxicity assays were conducted using the unicellular green microalga *Raphidocelis subcapitata*, the zooplankton organism *Daphnia magna* and the luminescent bacterium *Aliivibrio fischeri*. The bacterium *Escherichia coli* was assayed in a genotoxicity assay. The genotoxicity test consisted of the SOS Chromotest that determines DNA mutations in a genetically engineered *E. coli* strain (Environmental Bio-detection Products, Inc., Canada). A growth inhibition test with *R. subcapitata* was conducted in 96-well microplates in accordance with ISO 8692 2012. Plates were incubated for 72 h at 22 $^\circ\text{C}$ on a shaker at 70 rpm with continuous illumination (8,000 lx). Algal growth was measured as absorbance at 450 nm using a Thermo Multiskan Plate Reader (Thermo Scientific). Toxicity test with *D. magna* was conducted in accordance with ISO 6341 except that the test organisms were incubated individually in 24-well microplates (Nunc). The toxicological endpoint for *D. magna* was inhibition of mobility determined by inspection of the animals after 24 and 48 h (ISO 6341 2012). Toxicity test with *A. fischeri* was conducted in accordance with ISO 11348-1. *A. fischeri* was incubated in white 96-well plates (CulturPlate, Perkin Elmer) and changes in bioluminescence were quantified after 30 min using a Victor X2 Multilabel Plate Reader (Perkin Elmer).

Calculations and statistics

The toxicity response of the test organisms was expressed as inhibition (I) relative to control samples: $I = 1 - (R_i/R_c)$, where R_i and R_c are responses measured for inhibited and control samples, respectively. Concentration–response curves were fitted using a four-parameter inhibition model using iterative nonlinear regression:

$$I = m1 + \frac{(m2 - m1)}{\left[1 + \left(\frac{X}{\text{EC50}}\right)^{m3}\right]} \quad (1)$$

where I is the relative inhibition, X is the concentration of TWMP in mg/L, EC_{50} is the median effective concentration in mg/L, m_1 , m_2 and m_3 are model parameters (KalaidaGraph 5.0, 2023). The EC_{50} values from the different treatments were compared using the Wilcoxon rank sum test (Mann–Whitney U test) with a significance level of $p < 0.05$.

RESULTS AND DISCUSSION

Tire rubber microrubber particles

The TWMP used in the current study had a density of 1.16 g/cm^3 and varied in size from <1 to $130 \mu\text{m}$ and was dominated in numbers by particles with sizes $<100 \mu\text{m}$, and in weight by particles $>10 \mu\text{m}$ (Figure 2). This is in the same range as typical TWMP from tire abrasion found in the environment (Gieré & Dietze 2023). About 6 million tons of such tire wear material is released into the environment each year (Gieré & Dietze 2023).

Effect of UV treatment on the degradation of TWMP constituents

PAHs are examples of well-known toxicants present in tire wear. PAHs in TWMP leachates were degraded by UVC and VUV-UVC treatment (Figure 3). The concentration of pyrene, fluoranthene and benzo(a)pyrene decreased with increasing UV doses (Figure 3). About 57–79% of these PAHs were degraded by UVC treatment at 4.5 J/cm^2 (Figure 3(a)) whereas a combined VUV-UVC dose of 4.5 J/cm^2 degraded 86–90% (Figure 3(b)). The combined VUV-UVC dose of 4.5 J/cm^2 corresponded to approximately 0.9 J/cm^2 VUV and 3.6 J/cm^2 UVC. The degradation results for UVC are in the same range as reported previously for the removal of PAHs from wastewater (Rosinska 2021) whereas published results for noncatalytic PAH degradation by VUV are scarce. Interestingly, the initial pseudo-first-order rate constant for the removal of combined pyrene, fluoranthene and benzo(a)pyrene was about two times greater for VUV-UVC treatment compared to UVC treatment (Figure 3(d)). Pseudo-first-order reaction kinetics can be applied as a convenient model to facilitate the comparison of otherwise complex UV reactions in some batch and flow UV reactors (e.g., Shi *et al.* 2021). In the present study, the observed PAH degradation during the VUV-UVC treatment was likely due to a combination of direct UV photolysis mediated by photon absorption and then indirect photolysis mediated by reactive species produced by the VUV.

It should be noted that the concentrations of pyrene, fluoranthene and benzo(a)pyrene measured in the leachates shown in Figure 3 were above the aqueous solubility of these PAHs. The TWMP leachates were created by incubating tire microrubber particles in water followed by filtration through filters with a nominal pore size of $0.3 \mu\text{m}$. Hence, it is likely that the TWMP filtrate contained nano-size tire rubber particles ($<0.3 \mu\text{m}$) that contributed to the elevated PAH concentrations after extraction. Tire rubber particles are well-known sources of PAHs (Wagner *et al.* 2018; Gieré & Dietze 2023), and nanoparticles are good carriers of hydrophobic PAHs (Mahgoub 2019).

Organic additives in tire rubber leachates include phthalates and aromatic heterocyclic sulfur-containing compounds. Such compounds were also removed by VUV-UVC (Figure 4). In these experiments, known concentrations of DMP, DEP and BTZ were spiked into water samples (10 mg/L) and treated by the VUV-UVC flow system shown in Figure 1. The combined VUV-UVC treatment degraded about 34–70% of DMP, DEP and BTZ within 32 min corresponding to a UV dose of 16 J/cm^2

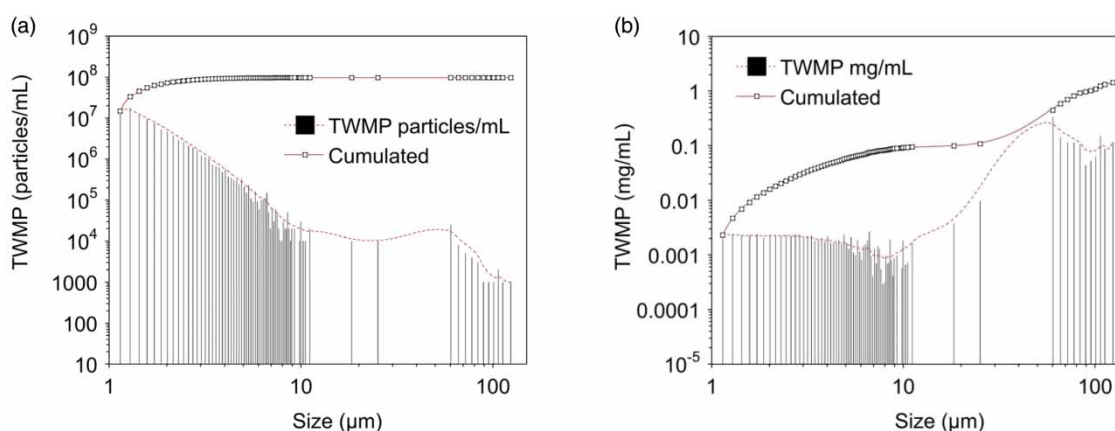


Figure 2 | Particle size (a) and weight (b) distribution for TWMP used in this study.

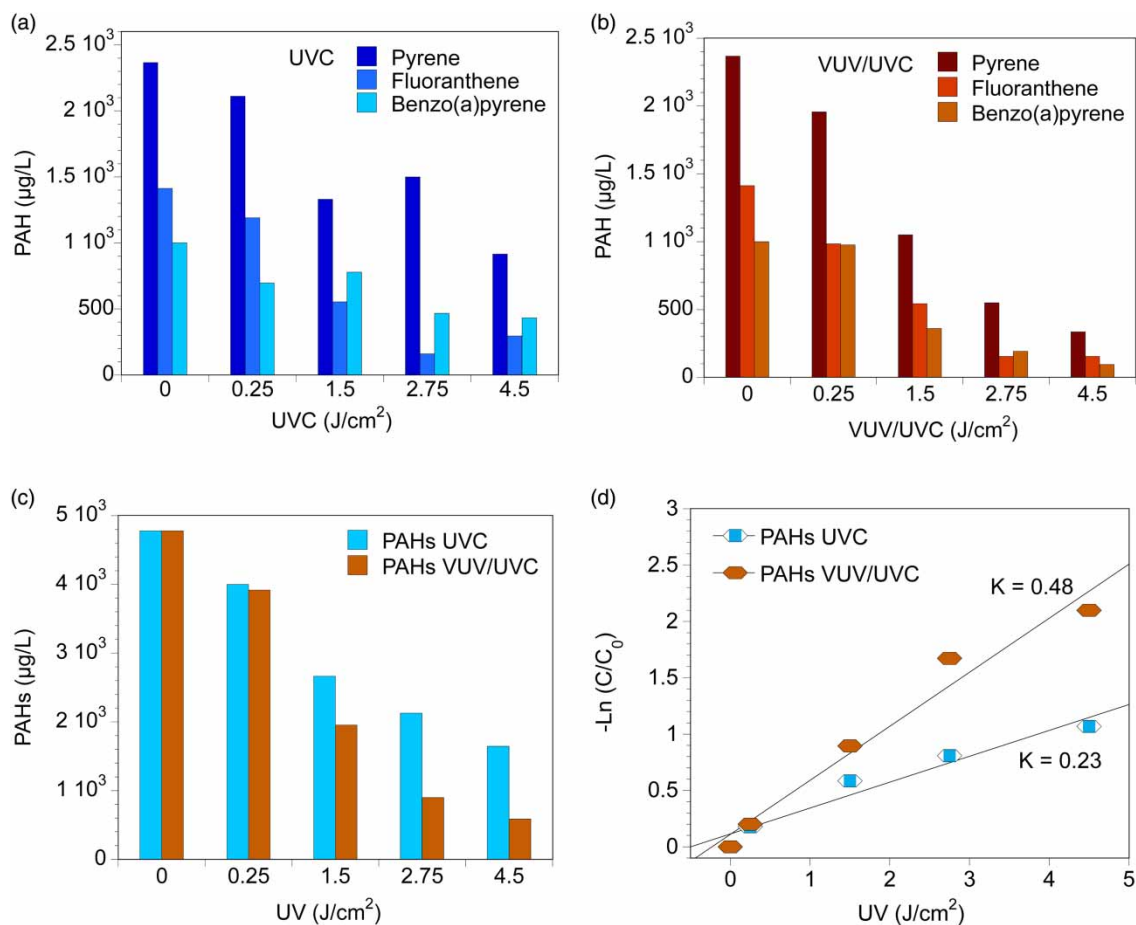


Figure 3 | Degradation of pyrene, fluoranthene and benzo(a)pyrene in TWMP leachates after UVC treatment (a), after VUV-UVC treatment (b), comparison of UVC and VUV-UVC degradation of the sum of pyrene, fluoranthene and benzo(a)pyrene ('PAHs') (c) and pseudo-first-order rate constants for UVC and VUV-UVC degradation of the three PAHs (d).

(Figure 4(b)). The pseudo-first-order rate constant for DMP and BTZ were somewhat comparable resulting in half-lives of 16–23 min. BTZ is added to tire rubber to accelerate vulcanization and enhance abrasion resistance and occurs in concentrations of more than 10 g/kg in TWMP. BTZ is also used in other industrial products than tire rubber and is therefore common in municipal wastewater and in surface waters (Lai *et al.* 2023). Conventional wastewater treatment plants often have incomplete removal of BTZ (e.g., 22–78%) but new water/wastewater AOP has a potential for more efficient BTZ removal (Yang *et al.* 2021; Lai *et al.* 2023). This study expands these observations by showing the degradation of BTZ by a VUV-UVC process without the addition of catalysts or oxidant precursors.

Zinc (Zn) was the dominant metal in the investigated TWMP leachates (0.5–1.6 mg/L). Elements such as magnesium (Mg), strontium (Sr), calcium (Ca), potassium (K) and sodium (Na) were also abundant in TWMP leachates (0.29–1.47 mg/L). This is in line with studies reporting zinc to be a dominant element in tire rubber with a mean mass fraction of 11.2 g/kg which corresponds to about 1% of the tire mass (O'Loughlin *et al.* 2023). Zinc and zinc oxide (ZnO) are added to tire rubber as a vulcanization accelerator to convert soft rubber into a stable product that can carry the weight of vehicles. The concentration of detectable zinc ions was affected by UVC and VUV-UVC treatment (Figure 4(d)). Quantification of zinc was based on ICP-MS analysis and a photometric method where Zn ions were complexed with 1-(2-pyridylazo)-2-naphthol. The ICP-MS analysis indicated that zinc was present in all samples and increased after UV treatment which may have been due to accelerated weathering of nano-size tire rubber particles in the leachates. UV weathering of tire rubber particles can mobilize metals and increase zinc concentrations in leachates (Simon *et al.* 2021). In contrast, the spectrophotometric 1-(2-pyridylazo)-2-naphthol method suggested that the concentration of free zinc ions decreased during the VUV-UVC treatment. Zinc was obviously not degraded, but a fraction appeared to be photochemically converted to a form that was less detectable by the

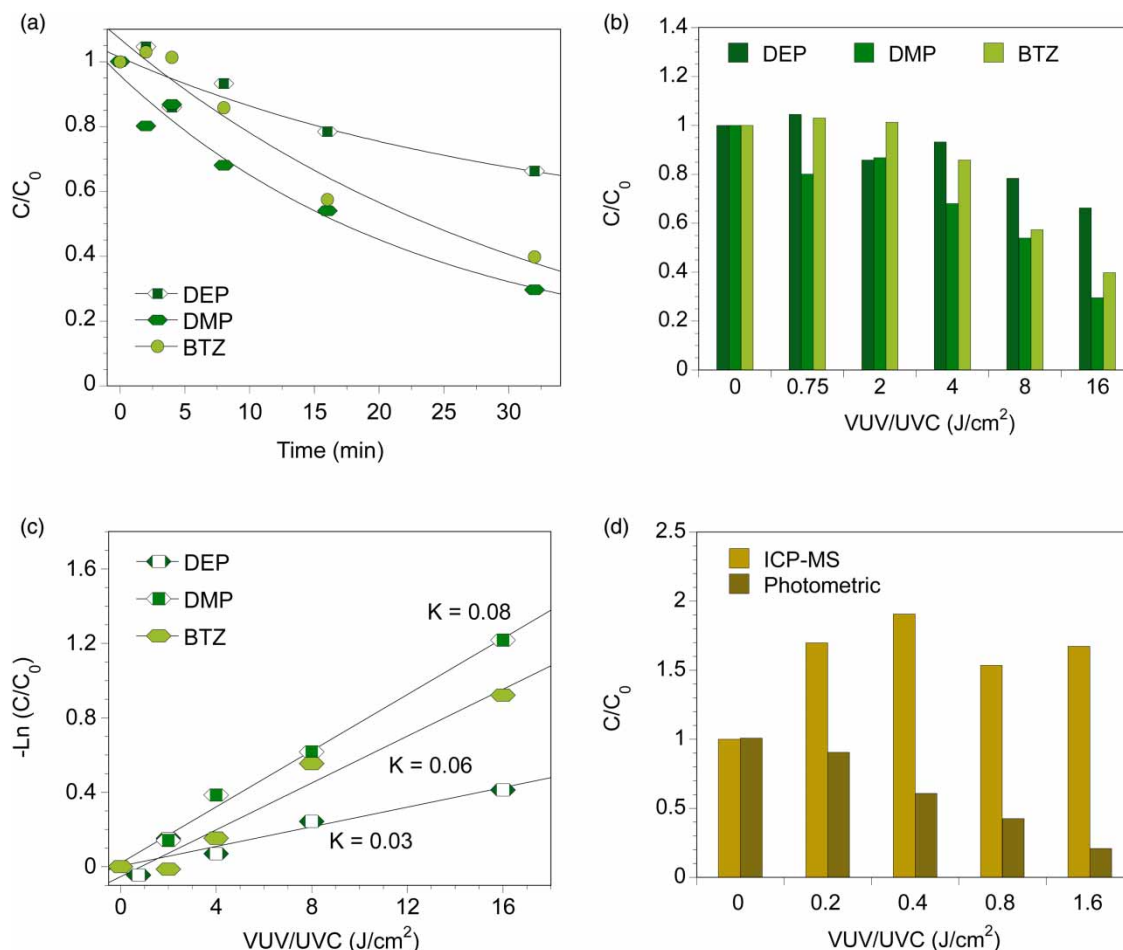


Figure 4 | Degradation of diethyl phthalate (DEP), dimethyl phthalate (DMP) and benzothiazole (BTZ) after VUV-UVC treatment as a function of irradiation time (a) and UV fluence (b). Pseudo-first-order rate constants for VUV-UVC degradation of DEP, DMP and BTZ (c). Changes in zinc concentrations measured by ICP-MS and photometry after VUV-UVC treatment (d).

traditional 1-(2-pyridylazo)-2-naphthol method. Undissolved or complex-bound zinc will not be detected by the 1-(2-pyridylazo)-2-naphthol method unless a pre-digestion is performed. This could suggest that the VUV-UVC treatment facilitated the complexation of some of the zinc ions.

Effect of UV treatment on toxicity of TWMP leachates

The ability of UV treatment to mitigate the ecotoxicity of TWMP leachates was assessed in bioassays with *R. subcapitata*, *A. fischeri* and *D. magna* (Figure 5). VUV-UVC treatment of TWMP decreased the toxicity to the freshwater microalga *R. subcapitata* (Figure 5(b)). UVC treatment alone showed a minor effect (Figure 5(a)). The traditional test organism *A. fischeri* was not inhibited by TWMP leachates and the concentration–response curve was therefore not fitted using Equation (1) (Figure 5(c)). The greatest concentration of TWMP leachates did not affect the luminescence or stimulate the metabolic activity of *A. fischeri* which may be partly due to the short 30 min incubation time used in this standard test (ISO 11348-1 2007). Hence, this suggests that acute tests with *A. fischeri* are not applicable for assessing the ecotoxicity of TWMP leachates. In contrast, the survival of the freshwater crustacean *D. magna* was negatively affected by TWMP leachates, but VUV-UVC treatment decreased the toxicity (Figure 5(d)). The relative mortality was somewhat comparable in raw (unfiltered) and filtered ($0 J/cm^2$) leachate and the toxicity in untreated samples increased with increasing exposure time (24 vs 48 h). However, treatment with 2.75 and 4.5 J/cm^2 VUV-UVC significantly ($p < 0.05$) decreased the mortality for *D. magna* exposed for 48 h to the TWMP leachate (Figure 5(d)). The relative mortality after 48 h was only 10% in samples treated with 4.5 J/cm^2 VUV-UVC which is comparable to the natural mortality in water samples without TWMP leachate.

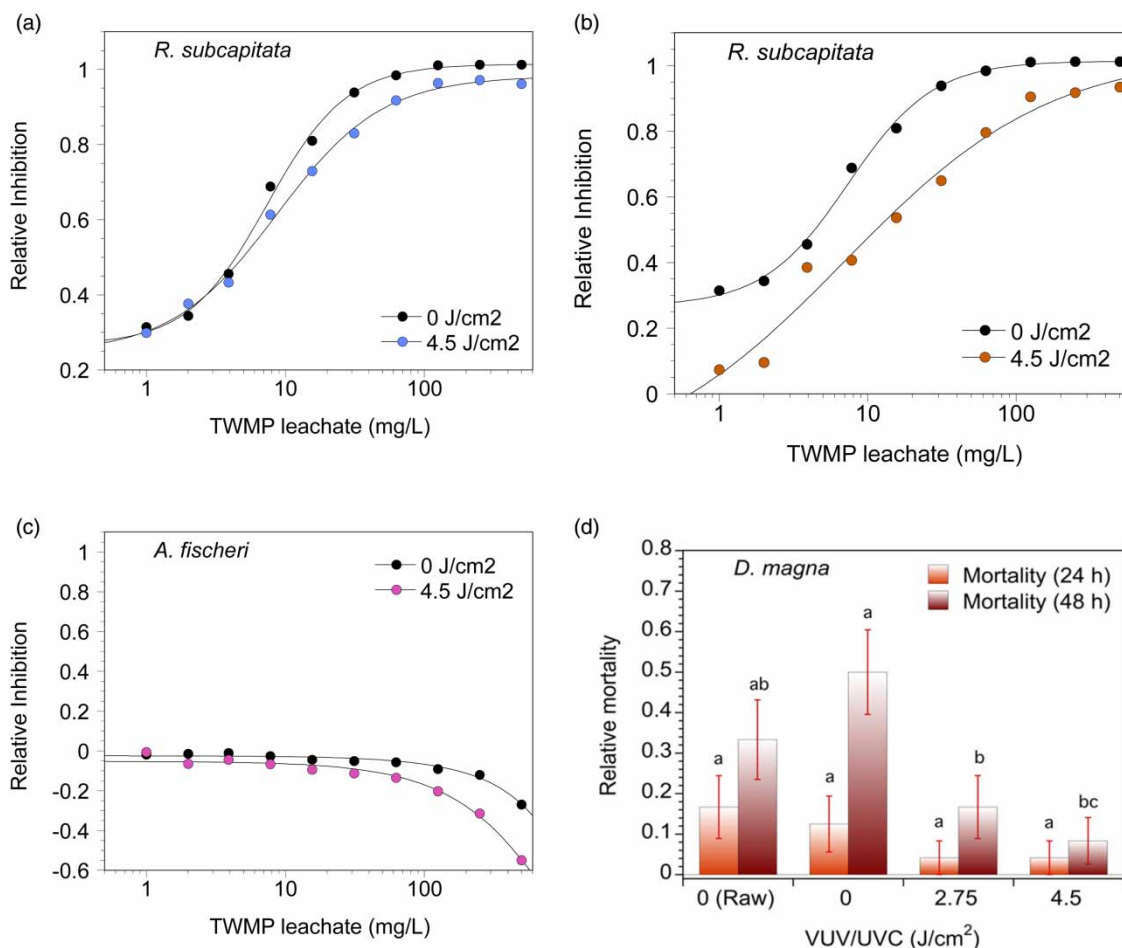


Figure 5 | Changes in toxicity of TWMP leachates to the green microalga *R. subcapitata* after 4.5 J/cm² UVC treatment (a), and after 4.5 J/cm² combined VUV-UVC treatment (b). Changes in toxicity of TWMP leachates to the luminescent bacterium *A. fischeri* after 4.5 J/cm² combined VUV-UVC treatment (c). The concentrations on the X-axes in (a–c) correspond to the amount of TWMP that was used to create the leachates. (d) The relative mortality of *D. magna* after 24 and 48 h exposure to TWMP leachates before and after VUV-UVC treatment ($n = 24$). A letter has been assigned depending on whether mortalities are significantly different from each other ($P < 0.05$).

The apparent genotoxicity of TWMP leachates was also attenuated by VUV-UVC treatment as indicated by an SOS test detecting DNA damage in a genetically engineered *E. coli* strain. Untreated TWMP leachates showed a weak genotoxic response whereas VUV-UVC treated TWMP leachates did not show any detectable genotoxic responses (data not shown).

In experiments with the freshwater microalga *R. subcapitata*, the median effective concentration (EC₅₀) for TWMP leachates was 1.67 ± 0.290 mg/L [\pm standard error; $n = 6$] (Figure 6). The traditional classification of hazardous substances considers compounds with EC₅₀ < 1 mg/L as ‘very toxic’ for aquatic life and substances with 1 mg/L < EC₅₀ < 10 mg/L as ‘toxic’ for aquatic life (United Nations 2021). Interestingly, the EC₅₀ value increased with increasing UV dose which suggests a decreasing toxicity (Figure 6). The toxicity decreased two- and five-fold after 4.5 J/cm² UVC and 4.5 J/cm² VUV-UVC treatment, respectively. This could be explained by the decreased concentrations of PAHs and organic additives in the TWMP leachates after VUV-UVC treatment (Figures 3 and 4). An attenuated concentration of bioavailable zinc (Figure 4(d)) and degradation of other TWMP constituents may also have been contributing factors. Regardless, the results suggested a potential for attenuating the ecotoxicity of TWMP leachates by VUV-UVC treatment and to a lesser extent UVC treatment (Figure 6). The efficiency of AOPs such as VUV-UVC in large-scale applications will depend on a range of factors such as the presence of other organic or inorganic constituents in the water (Duca et al. 2017). For example, the presence of elevated levels of organic matter as indicated by high COD levels can be a challenge for AOP processes because reactants are mainly consumed by other compounds than the target molecules (Andreozzi et al. 1999). Hence, it has been suggested that the best results will be obtained if COD levels are $\leq 5,000$ mg/L which may be achievable in some urban

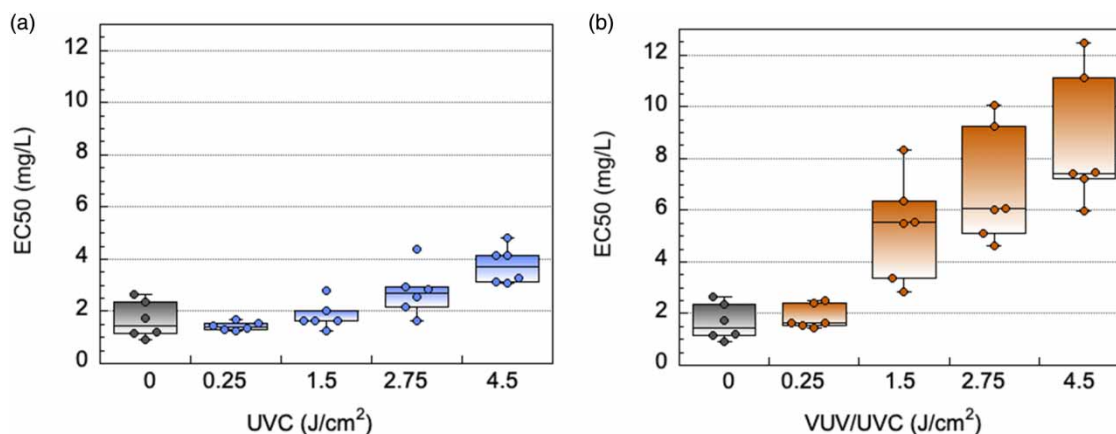


Figure 6 | Changes in toxicity of TWMP leachates to the green microalga *R. subcapitata* shown as median effective concentration (EC50) before (gray box) and after UVC treatment (a) and after combined VUV-UVC treatment (b). The horizontal line within each box represents the median values for six independent experiments and the upper and lower limits of a box represent the distance between the upper and lower quartiles (interquartile distance). Individual data points are shown as bullets ($n = 6$).

and industrial water systems (Andreozzi *et al.* 1999). The proposed VUV-UVC treatment could then have a potential for the treatment of water and wastewater from areas such as rubber industries (e.g., rubber manufactory plants, rubber recycling facilities), effluents from stormwater retention ponds and for polishing municipal wastewater effluents (tertiary treatment). VUV/UVC could potentially also be used to treat concentrated wastes from some of the facilities mentioned earlier.

CONCLUSIONS

A considerable amount of TWMP and their leachates eventually end up in stormwater, wastewater and surface waters. TWMP leachates contain a mixture of organic and inorganic constituents that are potentially toxic to aquatic life. This study investigated the effects of UVC and combined VUV-UVC treatment of TWMP leachates on compound removal and ecotoxicity. VUV-UVC treatment mitigated dissolved zinc and degraded common organic constituents in TWMP leachates. The potential ecotoxicity of leachates decreased after VUV-UVC treatment which was likely due to the formation of less toxic or less bioavailable transformation products. The study indicates the potential of VUV-UVC treatment as an advanced oxidation method to mitigate toxic compounds in TWMP leachates.

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DATA AVAILABILITY STATEMENT

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

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

- Andreozzi, R., Caprio, V., Insola, A. & Marotta, R. 1999 *Advanced oxidation processes (AOP) for water purification and recovery*. *Catalysis Today* **50** (10), 51–59. [https://doi.org/10.1016/S0920-5861\(99\)00102-9](https://doi.org/10.1016/S0920-5861(99)00102-9).
- Baensch-Baltruschat, B., Kocher, B., Stock, F. & Reifferscheid, G. 2020 *Tyre and road wear particles (TRWP) – a review of generation, properties, emissions, human health risk, ecotoxicity, and fate in the environment*. *Science of the Total Environment* **733**, 137823. doi:10.1016/j.scitotenv.2020.137823.
- Bolton, J. R., Beck, S. E. & Linden, K. G. 2015 Protocol for the determination of fluence (UV dose) using a low-pressure or low-pressure high-output UV lamp in bench-scale collimated beam ultraviolet experiments. *IUVA News* **17**, 11–17.

- Boucher, J. & Friot, D. 2017 *Primary Microplastics in the Oceans: A Global Evaluation of Sources*. IUCN, Gland, Switzerland, p. 43.
- Capolupo, M., Sørensen, L., Jayasena, K. D. R., Booth, A. M. & Fabbri, E. 2020 Chemical composition and ecotoxicity of plastic and car tire rubber leachates to aquatic organisms. *Water Research* **169**, 115270. doi:10.1016/j.watres.2019.115270.
- Del Puerto, O., Gonçalves, N. P. F., Medana, C., Prevot, A. B. & Roslev, P. 2022 Attenuation of toxicity and occurrence of degradation products of the fungicide tebuconazole after combined vacuum UV and UVC treatment of drinking water. *Environmental Science and Pollution Research* **29**, 58312–58325.
- Duca, C., Imoberdorf, G. & Mohseni, M. 2017 Effects of inorganics on the degradation of micropollutants with vacuum UV (VUV) advanced oxidation. *Journal of Environmental Science and Health Part A – Toxic/Hazardous Substances & Environmental Engineering* **52** (6), 524–532.
- Gieré, R. & Dietze, V. 2023 Tire-abrasion particles in the environment. *Advances in Polymer Science* **289**, 71–101. https://doi.org/10.1007/12_2022_118/FIGURES/9.
- Grigoratos, T. & Martini, G. 2014 *Non-Exhaust Traffic Related Emissions. Brake and Tyre Wear PM*. European Commission, Joint Research Centre, 26648 EN. doi:10.2790/21481.
- Halle, L. L., Palmqvist, A., Kampmann, K. & Khan, F. R. 2020 Ecotoxicology of micronized tire rubber: Past, present and future considerations. *Science of the Total Environment* **706**, 1–11. doi:10.1016/j.scitotenv.2019.135694.
- ISO 11348–1. 2007 *Determination of the Inhibitory Effect of Water Samples on the Light Emission of Vibrio fischeri (Luminescent Bacteria Test)*. International Standards Organisation, Geneva, Switzerland. Available from: <https://www.iso.org/standard/40516.html>.
- ISO 6341. 2012 *Water Quality – Determination of the Inhibition of the Mobility of Daphnia magna Straus (Cladocera, Crustacea) Acute Toxicity Test*. International Standards Organisation, Geneva, Switzerland. Available from: <https://www.iso.org/standard/54614.html>.
- ISO 8692. 2012 *Water Quality – Fresh Water Algal Growth Inhibition Test with Unicellular Green Algae*. International Standards Organisation, Geneva, Switzerland. Available from: <https://www.iso.org/standard/54150.html>.
- Kole, P. J., Löhr, A. J., Van-Belleghem, F. & Ragas, A. 2017 Wear and tear of tyres: A stealthy source of microplastics in the environment. *Environmental Research and Public Health* **14**, 1265. doi:10.3390/ijerph14101265.
- Lai, W. W. P., Lin, J. C. & Li, M. H. 2023 Degradation of benzothiazole by the UV/persulfate process: Degradation kinetics, mechanism and toxicity. *Journal of Photochemistry and Photobiology A: Chemistry* **436**, 114355. <https://doi.org/10.1016/J.PHOTOCHEM.2022.114355>.
- Lin, J., Yan, D., Fu, J., Chen, Y. & Ou, H. 2020 Ultraviolet-C and vacuum ultraviolet inducing surface degradation of microplastics. *Water Research* **186**, 116360. doi:10.1016/j.watres.2020.116360.
- Lu, F., Su, Y., Ji, Y. & Ji, R. 2021 Release of zinc and polycyclic aromatic hydrocarbons from tire crumb rubber and toxicity of leachate to *Daphnia magna*: Effects of tire source and photoaging. *Bulletin of Environmental Contamination and Toxicology* **107**, 651–656. doi:10.1007/s00128-021-03123-9.
- Mahgoub, H. A. 2019 Nanoparticles used for extraction of polycyclic aromatic hydrocarbons. *Journal of Chemistry* **2019**, 20. <https://doi.org/10.1155/2019/4816849>.
- O'Loughlin, D. P., Haugen, M. J., Day, J., Brown, A. S., Braysher, E. C., Molden, N., Willis, A. E., MacFarlane, M. & Boies, A. M. 2023 Multi-element analysis of tyre rubber for metal tracers. *Environment International* **178**, 108047. <https://doi.org/10.1016/j.envint.2023.108047>.
- Polyakova, O. V., Mazur, D. M., Artaev, V. B. & Lebedev, A. T. 2013 Determination of polycyclic aromatic hydrocarbons in water by gas chromatography/mass spectrometry with accelerated sample preparation. *Journal of Analytical Chemistry* **68**, 1099–1103. doi:10.1134/S106193481313008X.
- Rosinska, A. 2021 The influence of UV irradiation on PAHs in wastewater. *Journal of Environmental Management* **293**, 112760. doi:10.1016/j.jenvman.2021.112760.
- Shi, G., Nishizawa, S., Matsushita, T., Kato, Y., Kozumi, T., Matsui, Y. & Shirasaki, N. 2021 Computational fluid dynamics-based modeling and optimization of flow rate and radiant exitance for 1,4-dioxane degradation in a vacuum ultraviolet photoreactor. *Water Research* **197**, 117086. <https://doi.org/10.1016/j.watres.2021.117086>.
- Simon, M., Hartmann, N. B. & Vollertsen, J. 2021 Accelerated weathering increases the release of toxic leachates from microplastic particles as demonstrated through altered toxicity to the green algae *Raphidocelis subcapitata*. *Toxics* **9**, 185. <https://doi.org/10.3390/toxics9080185>.
- Sommer, F., Dietze, V., Baum, A., Sauer, J., Gilge, S., Maschowski, C. & Gieré, R. 2018 Tire abrasion as a major source of microplastics in the environment. *Aerosol and Air Quality Research* **18** (8). <https://doi.org/10.4209/aaqr.2018.03.0099>.
- United Nations. 2021 *Globally Harmonized System of Classification and Labelling of Chemicals (GHS)*, Ninth revised edn. United Nations, New York and Geneva. eISBN: 978-92-1-005213-9.
- Wagner, S., Hüffer, T., Klöckner, P., Wehrhahn, M., Hofmann, T. & Reemtsma, T. 2018 Tire wear particles in the aquatic environment – a review on generation, analysis, occurrence, fate and effects. *Water Research* **139**, 83–100. <https://doi.org/10.1016/J.WATRES.2018.03.051>.
- Wik, A., Nilsson, E., Kallqvist, T., Tobiesen, A. & Dave, G. 2009 Toxicity assessment of sequential leachates of tire powder using a battery of toxicity tests and toxicity identification evaluations. *Chemosphere* **77**, 922–927. doi:10.1016/j.chemosphere.2009.08.034.
- Yang, T., Mai, J., Wu, S., Liu, C., Tang, L., Mo, Z., Zhang, M., Guo, L., Liu, M. & Ma, J. 2021 UV/chlorine process for degradation of benzothiazole and benzotriazole in water: Efficiency, mechanism and toxicity evaluation. *Science of the Total Environment* **760**, 144304. <https://doi.org/10.1016/j.scitotenv.2020.144304>.
- Zoschke, K., Bornick, H. & Worch, E. 2014 Vacuum-UV radiation at 185nm in water treatment – a review. *Water Research* **52**, 131–145. doi:10.1016/j.watres.2013.12.034.