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Which factors mainly drive the photoaging of microplastics in freshwater?

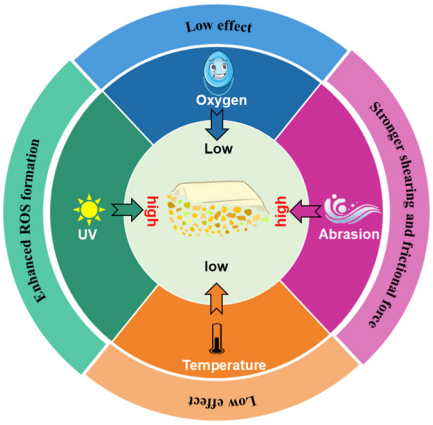
Jiamin Dai [a,1], Peng Liu [a,b,*,1], Chenyang Wang [a], Huang Li [a], Hong Qiang [a,b], Zeyuan Yang [a], Xuetao Guo [a,b,*], Shixiang Gao [c]

[a] College of Natural Resources and Environment, Northwest A & F University, Yangling 712100, China
[b] Key Laboratory of Plant Nutrition and the Agri-environment in Northwest China, Ministry of Agriculture, Yangling 712100, China
[c] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, China

HIGHLIGHTS

- Photoaging of polystyrene (PS) microplastics was different in various environmental factors.
- UV irradiation and mechanical abrasion were main contributors for the photoaging of PS.
- Oxygen and temperature showed low effects on the photoaging of PS.
- Various effects were critically related to ROS formation, UV absorption and physical stress.
- Light and physical abrasion working together on PS will cause more destructive effect.

GRAPHICAL ABSTRACT



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ABSTRACT

Light irradiation is considered as most important process for the aging of microplastics (MPs); however, which factors drive the process is still unknown. This study investigated the role of typical environmental factors including ultraviolet (UV), oxygen, temperature and physical abrasion in the photoaging of polystyrene (PS) in freshwater. Results showed that UV irradiation and abrasion were dominant factors for affecting photoaging of PS based on dynamic analysis in the property of MP itself and leachate. Especially, when both factors worked together on MPs, they caused more destructive effect. Mechanical exploration revealed that photoaging of MPs was mainly controlled by reactive oxygen species (ROS, $^1O_2$) generated from the reaction of dissolved oxygen/water molecules with polymer radicals initiated by UV energy. As an attacker on MPs, ROS formation was significantly linked with UV intensity, highlighting the important role of UV. The fragmentation was correlated to abrasion intensity, where a higher abrasion generated stronger physical force to tear MPs into fragments. The low roles of oxygen and temperature were presumably related to multiple effects of ROS formation and UV absorption. The findings firstly clarify the drivers in the photoaging of MPs, and contribute our effort to assess their fate and pollution risk in the environment.

1. Introduction

The ubiquitous plastic burdens in the global ecosphere raise an increasing concern (MacLeod et al., 2021). In addition to direct harm on organisms via entanglement and intestinal blockage (Gregory, 2009; Kühn et al.,

* Corresponding authors at: College of Natural Resources and Environment, Northwest A & F University, Yangling 712100, China.
E-mail addresses: pengliu@nwafu.edu.cn (P. Liu), guoxuetao2005@nwafu.edu.cn (X. Guo).
[1] Jiamin Dai and Peng Liu contributed equally to this work.

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2020), fragmentation of larger plastic debris by aging can produce substantial small plastic particles inducing additional emerging risk (Jahnke et al., 2017; Rocha-Santos and Duarte, 2015). Microplastics (MPs, generally defined as particles smaller than 5 mm), comprise the most abundant smallest fraction of plastic debris globally (Arthur et al., 2009; Lim, 2021), and have been received extensive attention in recent years due to their tiny size and huge amount (Lim, 2021; Vethaak and Legler, 2021; Zhang et al., 2020a). Once entering surface water, MPs readily undergo various aging processes including ultraviolet (UV) and heat irradiation, biodegradation, chemical oxidation and mechanical abrasion, etc. (Arp et al., 2021; Duan et al., 2021; Liu et al., 2021a), among which photoaging is considered as the most important process for environmental aging of MPs (Gewert et al., 2015). Numerous studies have investigated photoaging behaviors of MPs through laboratory-accelerated aging or outdoor exposure protocol (Luo et al., 2020; Shi et al., 2021; Wang et al., 2020; Zhu et al., 2020). These findings revealed important information that photoaging could not only alter the surface properties (particle size, morphology, hydrophobicity, and charge) of MPs, but also destroy the polymer chain and result in the release of MP-derived organic compounds.

Photoaging is an important process in the aging of MPs. Here, UV energy is received on the polymer, and then polymer radicals are formed, which further react with oxygen to form hydroperoxides. After a series of free radical reactions, the oxygen-containing functional groups are generated accompanying with the cleavage or cross-linking on polymer chains. In the real environment, the photoaging of MPs will be affected by various ambient factors, such as sunlight irradiation, dissolved oxygen, temperature and wave/tide slamming (Gewert et al., 2015; Hayes et al., 2017; Napper and Thompson, 2019). For example, the MP fragmentation frequently occurred on beaches, which is often accompanied by physical stress aging and thermo-oxidative during photoaging. Light energy and dissolved oxygen are the precursors for generating reactive oxygen species (ROS)—a main attacker on MPs (Zhu et al., 2020), which are the essential factors in the photoaging of MPs (Gewert et al., 2015). The ROS such as $O_2^{\bullet-}$ and OH• formed on MPs were the main culprits for inducing the formation of oxygen functional groups on MPs. Light irradiation intensity is greatest at sunny day possibly posing important effect on aging of MPs, but is lowest at sunless day or at night to show negligible effect. The effect of dissolved oxygen was also different limited by the different oxygen content in various water body and regions of the world, e.g. the lower oxygen content in eutrophic water than in normal water (Sukigara et al., 2021), and the thinner air with lower oxygen in high-attitude areas than in low-attitude areas. Similar case occurs on the effect of temperature, in which the surface temperature in the Death Valley, USA achieve as high as 93.9 °C (Records, 1913), but is significantly decreased to −98 °C in East Antarctic ice (Scambos et al., 2018). The physical stress is significantly correlated to the fragmentation of MPs, where the high abrasion from drastic wave and tide action of surface water may significantly enhance the fragmentation and cracking, while an opposite case occurs in still water surface layer (Duan et al., 2021; Wang et al., 2019). In addition, the physical stress can affect surface oxidation by altering the penetration of light energy and oxygen into deep layer of MPs due to the cracking and fragmentation (Song et al., 2017; Ter Halle et al., 2016). Based on these observations, these factors with different intensities will work together on photoaging of MPs, while which factors mainly drive the photoaging of MPs in aquatic environment is not fully understood up to now. Identifying and comparing the specific role of each factor in the photoaging of MPs is significant to deeply understand their aging behavior and assess their fate and pollution risk in the environment.

In this study, the photoaging of polystyrene (PS) MPs was investigated under various conditions from UV, oxygen, temperature and mechanical abrasion by exposure in ultrapure water and surface water from Weihe River. PS was selected as it was frequently detected in surface water, and PS exhibited significant photoaging properties (Elizalde-Velázquez and Gómez-Oliván, 2021). The surface properties including photooxidation, fragmentation and morphology variations of PS and leachate properties including pH, total organic carbon (TOC) and photoluminescence (PL) were investigated. The carbonyl index (CI) and particle size were calculated from Fourier transform infrared (FTIR) spectroscopy and particle counting in scanning electron microscopy (SEM) images, respectively to quantitatively compare photoaging degrees among various treatments. Also, the mechanisms regarding the effects of various factors on photoaging of MPs were unravelled via electron paramagnetic resonance (EPR) measurement of ROS in various treatments. Finally, the real photoaging behavior of PS MPs in Weihe River surface water was revealed. The results obtained in this study will improve understanding of the aging, fate and pollution risk of MPs in aquatic environments.

2. Materials and methods

2.1. Materials

PS MPs in granule forms were purchased from Zhongcheng Plastic factory (Guangzhou, China), which were sieved to produce a fraction of MP particles with average size of 107.1 ± 14.3 μm. 5,5-dimethyl-1-pyroline-N-oxide (DMPO, >97 %), dimethyl sulfoxide (DMSO, AR) and 2,2,6,6-tetramethylpiperidine (TEMP, 98 %) were obtained from J&K Chemical (Beijing, China). The freshwater sample was collected from October 2020 from Weihe River (108°6′E, 34°14′N) (Fig. S1), where MPs had been previously detected (Bian et al., 2022; Ding et al., 2019). Freshwater samples were filtrated through 0.22 μm membrane to remove suspended substances.

2.2. Photoaging tests on various environmental factors

Photoaging experiments were conducted in a UV chamber equipped with four UV lamps (254 nm, 160 W) by adding PS MPs in 150 mL quartz conical flask (details were described in Text S1). UV irradiation at 254 nm was selected mainly to simulate the accelerated photoaging of MPs in water, which were widely adopted in previously laboratory aging tests (Huang et al., 2021). To investigate the effects of various factors (i.e. light, oxygen, temperature and mechanical abrasion), three different groups including low, medium and high intensity were setup (as shown in Fig. S2). As for light, the 0, 2 and 4 lamps were turned on to represent the low, medium and high intensity (0, 266 and 532 $\mu W/cm^2$) of light irradiation. As for oxygen, the solutions were ventilated with nitrogen and oxygen in the whole photoaging reaction representing the low and high oxygen contents, respectively, and the flask without sealing denoted the medium oxygen content. Correspondingly, the temperatures with three intensities were conditioned by adding ice packs in water bath or elevating stirrer temperature to achieve the temperatures at ~0 and 50 °C, respectively. The group with no treatment represented medium temperature (~30 °C). The agitations with 10, 300 and 600 rpm were setup by adjusting the stirrer speed to represent physical abrasions with different intensity from wave or tide action. These value ranges of factors represented the environmental conditions from natural to extreme cases (Liu et al., 2021a). Based on Guinness World Records, the highest surface ground temperature was as high as 94 °C in the Death Valley, California (Records, 1913). Wu et al. (2021) used 700 rad/min (~117 rpm) of mechanical stirrer to simulate natural water velocity (2.11 m/s) of Dongting Lake, China. The high UV (4 lamps), medium oxygen (air), temperature (~30 °C) and abrasion (300 rpm) were set up unless one certain factor was investigated, as described in the following text and figures. Here, when a particular factor is the object of study, the rest of the elements are fixed.

2.3. MP characterization and filtrate analysis

Surface morphologies of virgin and photoaged PS MPs were characterized by field-emission SEM (NanoSEM 450, FEI). The particle sizes were obtained by counting the particles in SEM images using Nano Measurer software (version 1.2.5, Fudan University). Surface oxidation and functional groups on virgin and photoaged PS MPs were examined by FTIR spectroscopy (Vetex70, Bruker). The leachate properties including solution pH, TOC and excitation-emission matrices (EEM) were analyzed

by pH meter (PB-10, Sartorius), TOC analyzer (TOC-L, Shimadzu) and spectrofluorophotometer (RF-6000, Shimadzu), respectively.

2.4. EPR measurement

Details on determination of environmentally persistent free radicals (EPFRs) and ROS (OH•, $^1O_2$ and $O_2^{\bullet-}$) in photoaging by various factors were provided in Text S2.

2.5. Statistical analyses

All statistical analyses were conducted using IBM SPSS (version 20.0) software. The changes in CI and particle size among photochemical treatments by various factors, and in TOC and PL intensity in leachate from photoaged PS MPs in ultrapure water and freshwater were statistically compared using a one-way analysis of variance (ANOVA), followed by Duncan's test. Pearson correlation analysis was performed to determine the important factors in photoaging of MPs. An effect with $p \geq 0.05$ and $^*p < 0.05$ and $^{**}p < 0.01$ was considered not significant (NS) and significant (denoted as a, b, c, d), respectively.

3. Results and discussion

3.1. Photoaging behavior on various environmental factors

3.1.1. Short-term photoaging behavior

FTIR spectra were obtained after 5 d of irradiation to compare the role of various environmental factors in the photoaging of PS MPs (Fig. S3). Compared to original sample, new peak at 1650–1800 cm^{-1} assigned to carbonyl group was detected in the infrared spectra of all UV-irradiated samples except for the dark-treated ones (Liu et al., 2021b; Yang et al., 2018). In addition, the spectra at 1168–1314 cm^{-1} became swelled after UV irradiation, suggesting the generation of functional group (C—O) in treated PS MPs (Hayes et al., 2017). In addition to dark treatment, it can also be observed the few change in infrared spectra of low-temperature treated PS compared to original ones (Fig. S3c), which potentially revealed the low effect of low temperature on photoaging of PS MPs.

In order to quantitatively describe and compare the photooxidation degrees of PS MPs among various treatments, the CI values were calculated by the absorption intensity at carbonyl to methyl (reference peak) (1740/1451) in FTIR spectra (Song et al., 2017). Based on ANOVA analysis, the CI values of PS MPs on all of the treatments (0.23–0.36) were significantly increased compared to that in original ones (0.10), except for the case in dark treatment (shown in Fig. 1). Also, the CI values exhibited different alteration profiles among environmental factors with different intensities. As for UV irradiation, the CI values were positively increased with UV intensity. After 3 d of irradiation, the CI value in high UV exposure was significantly higher than that in medium UV, and both of groups were further significantly higher than that in low UV (Fig. 1a), which indicated the important role of UV energy in the photooxidation of PS MPs. Although the CI values were also positively related to the oxygen contents, there was no significant difference among low, medium and high treatment groups (Fig. 1b). As for temperature, both low and high temperatures were seemingly not conducive to the photoaging of PS MPs (Fig. 1c). Low temperature might decrease migration rate of molecules and electrons, further inhibiting the photooxidation of MPs. In a high temperature, we observed that the solution became darker than other systems (Fig. S4), in which might shield UV energy to the surface of MPs and decrease their absorption efficiency for UV. Increasing abrasion significantly enhanced the photooxidation of PS from low (10 rpm) to medium intensity (300 rpm), while the enhancement was not obvious with a further increased abrasion (from 300 to 600 rpm) (Fig. 1d). This might be ascribed to that the enhanced

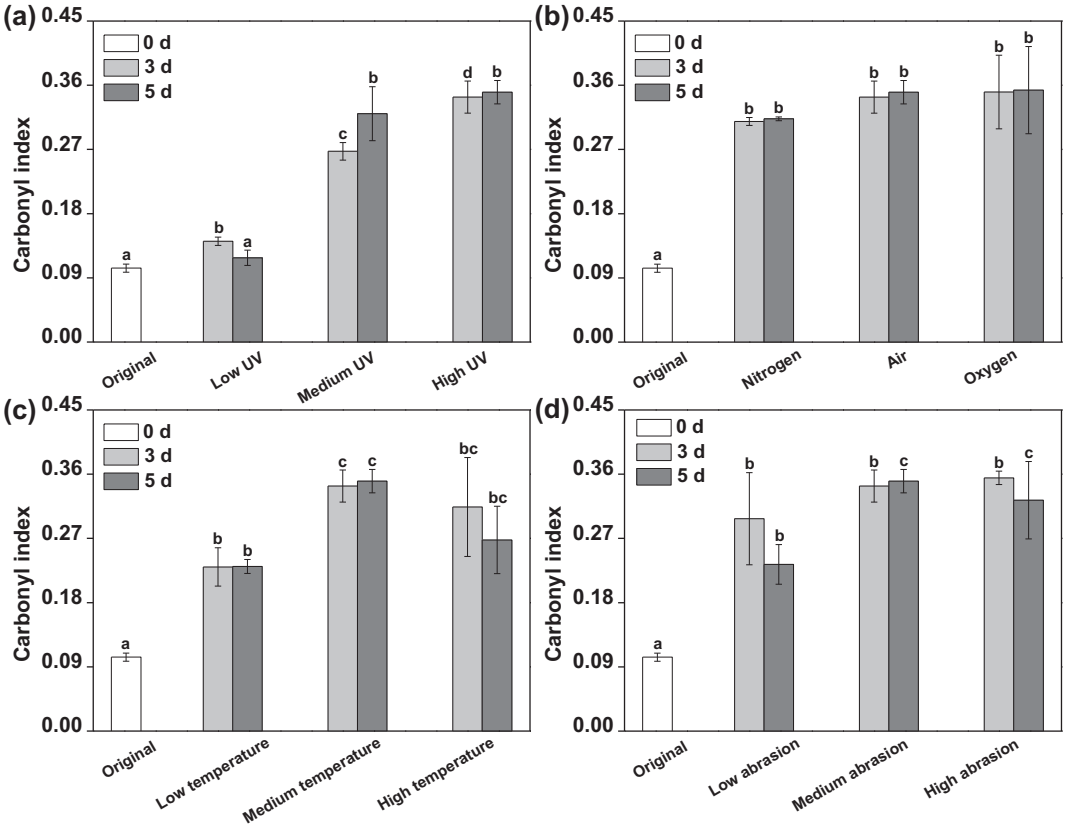

Fig. 1. Carbonyl index (CI) of PS MPs in various photochemical treatments of environmental factors: (a) UV, (b) oxygen, (c) temperature and (d) mechanical abrasion (data were analyzed by one-way ANOVA followed by Duncan's test; groups with different letters indicate significant difference ($p < 0.05$) among various treatments; the high UV (4 lamps), medium oxygen (air), temperature (~30 °C) and abrasion (300 rpm) were set up unless one factor was investigated, as described in the following figures).

dispersion in solution caused by physical agitation could increase the absorption efficiency of UV energy by MPs, while a higher physical agitation suggested highly increased mechanical abrasion and significantly enhanced the fragmentation of MPs to expose many more fresh surfaces that might decrease the CI values (Song et al., 2017).

Photoaging of MPs also accompanied the fragmentation and surface cracking. As shown in Fig. 2, PS MPs underwent various extents of fragmentation among different treatments. The lowest extent of fragmentation occurred on dark, low temperature and abrasion groups after 5 d of treatments, where average sizes were only decreased by 15.7 %, 0 % and 0.77 %, respectively, similar to the results in CI values (Fig. 1). Correspondingly, the high temperature and abrasion treatments exhibited the highest fragmentation, such as 65.6 % and 68.1 % of decrease in particle sizes after 5 d (Fig. 2c, d). As for UV irradiation, a gradual decrease of average sizes was observed with light intensity. For example, 59.2 % of decrease in particle sizes occurred in high UV intensity relative to the original ones. Overall, the UV, physical stress and temperature were seemingly dominant factors responsible for the fragmentation of PS MPs. Because absorbing UV energy is the premise of photodegradation of MPs, the higher the UV intensity, the higher the absorption efficiency of MPs for UV, and the faster the MPs photooxidized and fragmented (Singh and Sharma, 2008). The importance of mechanical abrasion in the fragmentation could be explained by the physical force and tensile strength of MPs, where the increased physical agitation suggested the higher shearing force from water and frictional force from particles posed on MPs, which could tear MPs with big sizes to small fragments (Ren and Ni, 2021; Song et al., 2017). As for the effect of temperature, high temperature suggested the co-occurrence of photo and thermal aging, enhancing the fragmentation of PS MPs (Singh and Sharma, 2008). However, the relatively low enhanced fragmentation from medium to high temperature suggested an unimportant role of thermal aging. The effect of temperature mainly depended on the enhanced movement of molecules and ROS-involved reaction rate caused by increased temperature seen from the significantly enhanced fragmentation from low to medium temperature (Singh and Sharma, 2008). From Fig. 2b, the particle sizes changed little among low, medium and high oxygen contents, revealing a relatively small role of oxygen in the photoaging of PS MPs. Theoretically, the oxygen should be a major contributor for the photoaging of MPs because it is the precursor of ROS that mainly attacked MPs (Gewert et al., 2015; Zhu et al., 2020). In our study, the effect of oxygen might be relatively low by comparing the data results of nitrogen, oxygen and air. In other words, a few amount of oxygen could achieve a higher photoaging degree of MPs if other factors such as light irradiation and mechanical abrasions were met. Here, a few of dissolved oxygen could rapidly react with polymer radicals to form ROS. Because the formation of ROS was also related to the generated polymer radicals, a higher oxygen content provided by oxygen-pumping system not necessarily produced many more ROS (Gewert et al., 2015). However, the oxygen pump operation causes the gas to disperse into the liquid layer through the small pores in the engineering while increasing the contact area between the gas-liquid two phases. The oxygen bubbles might also exhibit certain inhibition on fragmentation of MPs since the generated bubbles could adhere some particles from solution to gas-liquid interface and even in air (Zhang et al., 2020b), decreasing the chemical attack of ROS on MPs, despite the assumption required to be further validated. PS MPs after 3 d of treatments showed a similar but low fragmentation compared to 5 d of treatments (Fig. S5).

The results in size distribution showed a similar trend with those in average size (Fig. S6). However, different from the formation of many particles with smaller size (<20 μm) and bigger size (>100 μm) in other groups, many more fragmented particles have size ranges within 20–90 μm, with no particles smaller than 20 μm or bigger than 100 μm in high-oxygen treated group (Fig. S6b). This indicated that oxygen might pose inhibiting

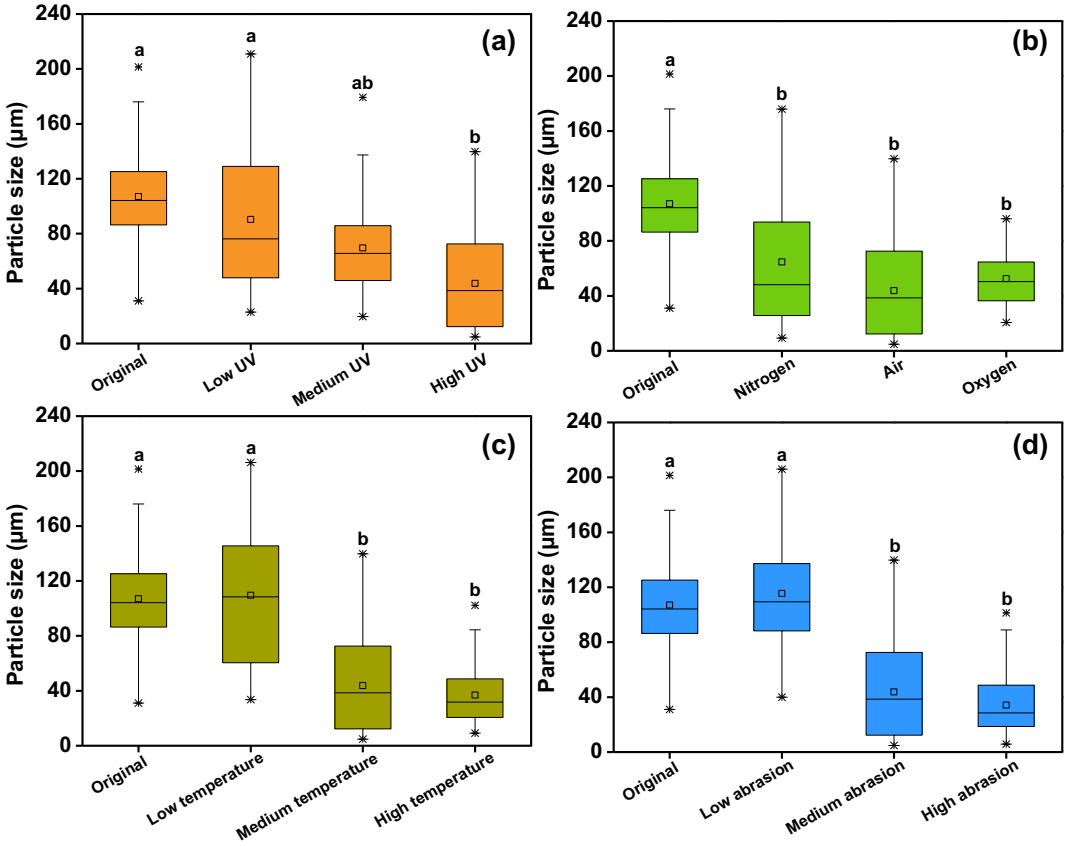

Fig. 2. Particle size of PS MPs after 5 d of photochemical treatments by various environmental factors: (a) UV, (b) oxygen, (c) temperature and (d) mechanical abrasion (the transverse lines from top to bottom in boxplot represent the maximum value, 75 % percentile, medium value, 25 % percentile and minimum value; asterisks outside the box represent the abnormal value).

effects on the further fragmentation of generated medium-sized particles. Normally, the fragmentation normally was occurred along with cracking in the surface of plastics, resulting in smaller fragments, and the fragmentation was mainly caused by chemical attack from ROS (Ter Halle et al., 2016). Therefore, it could be speculated that excessive oxygen interfered the ROS formation and/or inhibited the contact of ROS with surface of fragmented particles, validating the speculation regarding the adhesion of particles on oxygen bubbles. SEM images revealed that virgin PS MPs in granular forms were changed into fragmented pieces with different sizes after 5 d of irradiation in high-intensity treatment groups (Fig. S7), indicating the morphological alterations.

3.1.2. Long-term photoaging behavior

In order to describe the effect of environmental factors on the long-term photoaging behavior, 15 d of irradiation treatments were conducted. Compared to the short-term irradiation (5 d), long-time treatments enhanced the photoaging (surface oxidation and fragmentation) of PS MPs more significantly (Fig. S8). However, different cases occurred in high UV and temperature treatment groups, where the CI values decreased from 0.35 and 0.27 of 5 d-irradiated PS to 0.31 and 0.24 of 15 d-irradiated ones shown in Fig. 1a,c and Fig. S8a. The possible explanation was that the fragmentation of MPs exposed new surface, which decreased the overall surface oxidation (Liu et al., 2019; Song et al., 2017). However, this was not appropriate for the high-temperature treated ones because no fragmentation occurred from 5 d to 15 d (from 36.8 ± 8.11 μm to 39.0 ± 9.11 μm) (Fig. 2c and Fig. S8b). This might be related to the high temperature-induced darker solution as stated in Section 3.1.1. Since the photodegradation rate was affected by the incident light available, it was independent of the inherent photoreactivity of the plastics (Nelson et al., 2021). The dark solution severely sheltered the MP particles in quartz flask from UV light, resulting in the pause of photo-initiated reaction and following inhibition on photoaging of PS MPs.

As for various environmental factors in long-term irradiation, their effects on the photooxidation of PS MPs followed a similar order with those in short-term irradiation. As shown in Fig. S8a, the CI values in medium and high UV irradiation were significantly higher than that in low UV irradiation, while no significant difference in CI values occurred among oxygen, temperature or abrasion with different intensities, indicating more important role of UV in the photooxidation of PS MPs. On the basis of particle sizes, UV and mechanical abrasion contributed for the more significant fragmentation of PS MPs, seen from 61.5 %, 38.7 %, 49.5 % and 89.9 % of decrease in particle sizes in high-intensity UV, oxygen, temperature and abrasion groups compared to those in low-intensity treated ones. These results suggested that light irradiation and mechanical abrasion were the dominant factors for affecting the photoaging of MPs, at least PS MPs in aquatic environments. Moreover, only when these two factors worked together on MPs, they could cause more destructive effect (shown in Fig. S8b). In other words, the photoaging of MPs, especially fragmentation was slow in no sun day or sun day with no wind and wave, but became obviously fast in the day with sunlight and stormy wave. The findings are significant for understanding the drivers and limiting factors in the photoaging of MPs and assessing their fate and pollution in the environment. We believe that this is the first report to identify the role of typical environmental factors in the photoaging of MPs.

3.2. Leachate properties on various environmental factors

Photoaging resulted in the chain scission of polymer and release of low-molecular products into leachate (Dees et al., 2021; Gewert et al., 2018; Shi et al., 2021). The leachate properties (e.g. pH, TOC and PL) were analyzed to further compare the effects of various factors on photoaging of PS MPs. TOC results showed that the contents were positively increased with the treatment intensity within 5 d, suggesting the release of low-molecular organic products and effects of environmental factors. A higher TOC content from original PS MPs might be ascribed to the exfoliation of unpolymerized monomer and organic additives that were physically incorporated in PS polymer (Lee et al., 2021). As for treatment groups, the TOC contents decreased from 5 d to 15 d for most of groups, especially the medium- and high-intensity treatments, which might be ascribed to the mineralization of organic products generated initially (Shi et al., 2021). Moreover, the mineralization that normally denoted the conversion of organic compounds to inorganic components, might further be included the water, salts and minerals. However, the explanation was not appropriate for the decrease in TOC for dark system since no UV light was involved. This might be the re-sorption of dissolved organic chemicals on aged PS MPs as indicated by our previous study (Liu et al., 2020). Release of organic products also caused the decrease in leachate pH for all of the treatments but with different extents (Fig. S9). Among these factors, the most significant decrease occurred on UV and mechanical abrasion, e.g. 56.9 and 23.2 % of decrease in solution pH under high-intensity UV and abrasion groups compared to those in corresponding low-intensity treated ones, which were consistent with the discussions in surface photoaging properties in Sections 3.1 and 3.2.

EEM analysis revealed that compared to original sample, new PL signals were detected in leachates of 5 d-treated PS MPs with the maximum excitation (Ex) at 210–275 nm and emission (Em) at 420–450 nm, except for dark and low abrasion groups (Fig. S10). These photoluminescent organic chemicals were assigned to photoinduced humic-like components that mainly derived from the chain scission and oxidation of PS polymer based on previous reports (Lee et al., 2020; Tian et al., 2019). Lee et al. (2020) showed that the peak in fluorescence regions at (Em) 350 to 550 nm was assigned to the humic-like components from aged filtrates. In order to quantitatively compare the relative contents of photoluminescent products among various treatments, the maximum PL intensity at ~255/450 nm (Ex/Em) was picked up and plotted in Fig. 3b. Obviously, the PL intensity for original sample and dark-treated ones was significantly low (81 and 38–126). By comparison with higher TOC data, it could be validated that the organic chemicals from these two systems were not chain-scission products from PS MPs, but more likely to be the unpolymerized monomer or additives. From Fig. 3b, the PL intensity was rapidly increased for UV irradiation with different intensities within 5 d (2540–4730), suggesting the continuous chain scission and oxidation and release in leachate. Similar results could be observed in the treatments of oxygen, temperature and abrasion despite with different PL intensities (Fig. 3b). However, the decreased PL intensity from 5 d to 15 d of partial treatments indicated the degradation of released photoluminescent organic products, similar to the TOC analysis. The re-adsorption of organics was not the main cause, because electrostatic repulsion occurred on the negatively charged photoluminescent organic products and MPs.

3.3. Relationship between environmental factors and photoaging properties of MPs

The correlations between environmental factors and photoaging properties (denoted as CI value, particle size, PL intensity and TOC) were established using Pearson correlation analysis to attempt to determine which factors mainly drive the photoaging of MPs in water. Here, the red or blue color indicates the positive or negative correlation, and the darker the color, the greater the correlation (Fig. 4 and the data in Table S1). Among these factors, UV showed the darker red color indicating significant positive correlations with CI values (an index characterizing photooxidation degree) than oxygen, temperature and mechanical abrasion (Pearson's coefficients of 0.849–0.930, 0.711–0.814, 0.389–0.649 and 0.601–0.791 on UV, oxygen, temperature and mechanical abrasion, respectively in Table S1). This indicated the most important role of UV but less important effect of temperature in photooxidation of PS MPs. Based on particle sizes, mechanical abrasion exhibited a strong negative correlation (Pearson's coefficients of –(0.842–0.931), $p < 0.01$). Because the decreased particle sizes suggested the increased fragmentation of MPs, the higher negative correlation indicated the more important effect of mechanical abrasion. As for the release of organic compounds (PL and TOC) in leachate, the degrees of influence followed the general order of UV > mechanical abrasion

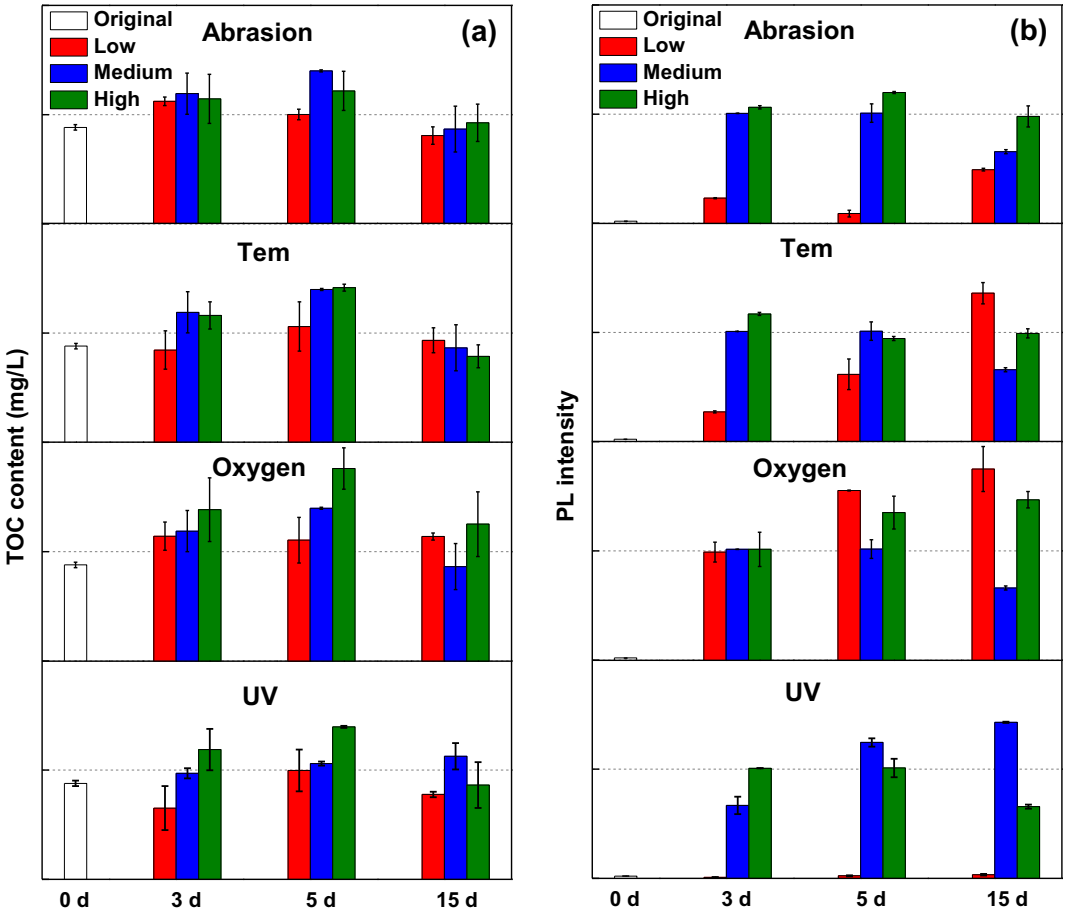

Fig. 3. (a) TOC content and (b) PL intensity of leachate released from photoaged PS MPs in various treatments of UV, oxygen, temperature and mechanical abrasion (each tick in *y* axis of figure denotes 1000 and 3800 for TOC and PL intensity, respectively).

> oxygen > temperature, consistent with the results in surface photoaging property of MPs. (Song et al., 2017) reported that combining UV and mechanical abrasion resulted in significant fragmentation of PE, PP and PS MPs, similar to our results. (Jahnke et al., 2017) reviewed that the natural aging of plastics/MPs were affected by various factors including physical stress caused by wave action and other particles, temperature fluctuations, UV and microbial degradation, etc. Previous studies suggested the important effects on environmental factors in photoaging of MPs, while the findings here evidenced the importance of UV light and physical abrasion among various other environmental factors in aging of MPs.

3.4. ROS-mediated mechanisms by environmental factors

Here, we intended to explain the relevant mechanisms for controlling the photoaging of PS MPs. The reactive species including EPFRs and ROS (OH•, $O_2^{\bullet-}$ and $^1O_2$) were investigated in dark, nitrogen, high temperature and low abrasion groups to compare with that in high UV with medium oxygen, temperature and abrasion group (expressed as air in following). As shown in Fig. 5a, no signal was detected in EPR spectra of PS MPs in dark condition, while distinct EPR signals could be observed in UV irradiation systems, suggesting the formation of EPFRs in UV but not in dark condition. As for various UV irradiation treatments, it could be observed that the intensity of EPFR signal in air system was relatively stronger than those in nitrogen, high temperature or low abrasion condition, potentially indicating that many more EPFRs were generated in air condition, in accordance with the results in CI and particle size that higher photooxidation and fragmentation occurred in air than in nitrogen, high temperature and low abrasion groups (Figs. 2 and 3). As reported, EPFRs with inherently low activity and relatively stable possessed a low ability for directly oxidizing MPs, while they could react with dissolved oxygen to yield ROS via electron transfer (Zhu et al., 2020). Fig. 5b showed that a 3-line EPR signal with an intensity of 1:1:1 assigned to $^1O_2$ was detected in the leachates of all systems including UV and dark. The signal in dark might be ascribed to the response of TEMP and its products (Nardi et al., 2014). Further comparisons showed that the signal intensity in dark and nitrogen conditions were relatively lower than those in air, high temperature and low abrasion conditions. This suggested higher production of $^1O_2$ in several latter systems, signifying the higher photoaging rates of PS MPs in these systems. However, the results indicated that $^1O_2$ was not the only ROS responsible for photoaging of PS MPs, and there might be other ROS effects, because the CI values of PS MPs in nitrogen were higher than those under high temperature and low abrasion, and showed higher fragmentation than those under low abrasion treatment. Surprisingly, EPR spectra of OH• and $O_2^{\bullet-}$ showed that no any signal was detected in leachates from all UV and dark systems (Fig. 5c, d), inconsistent with previous reports. In current study, the higher photoaging characteristics of PS MPs in UV irradiation suggested that there should be one or more species with high oxidizing potentials produced. For example, OH• had a high oxidation potential of 2.8 V and thus had a very strong oxidative ability to degrade various organic pollutants in water (Shi et al., 2022). Zhu et al. (2020) detected obvious OH• and $O_2^{\bullet-}$ signals in xenon lamp irradiation of PS MPs, as also indicated by the studies of (Ding et al., 2022) and (Wang et al., 2022). In addition to the role of $^1O_2$, the possible explanation for above phenomenon might be the generation of other free radicals possibly due to the incorporation of additives and impurities in plastics (Kaczmarek et al., 2000; Khaled et al., 2018), though many more evidences were required to validate the speculation. In addition to above speculation, the low detection of OH• and $^1O_2$ by the instrument might also be a cause, which needed to be explored further.

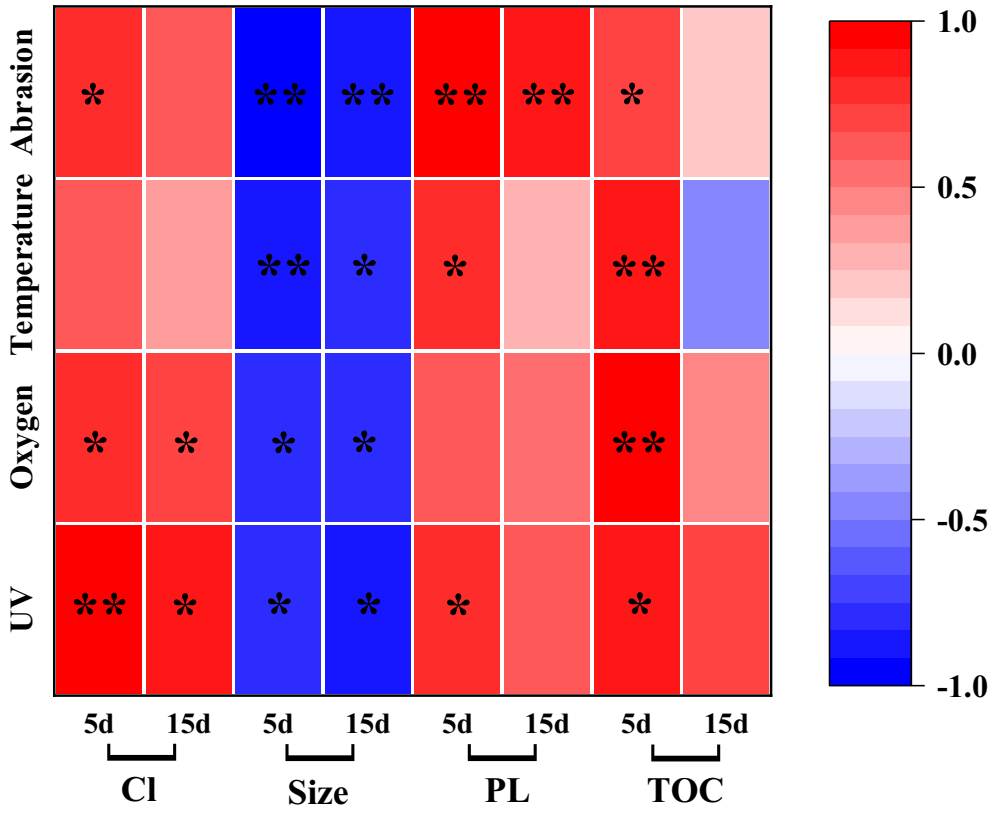

Fig. 4. Pearson correlation analysis between environmental factors (UV, oxygen, temperature and mechanical abrasion) and photoaging properties of PS MPs (the red or blue color indicates the positive or negative correlation, and the darker the color, the greater the correlation. $^{*}p < 0.05$ and $^{**}p < 0.01$ were considered as a statistically significant difference).

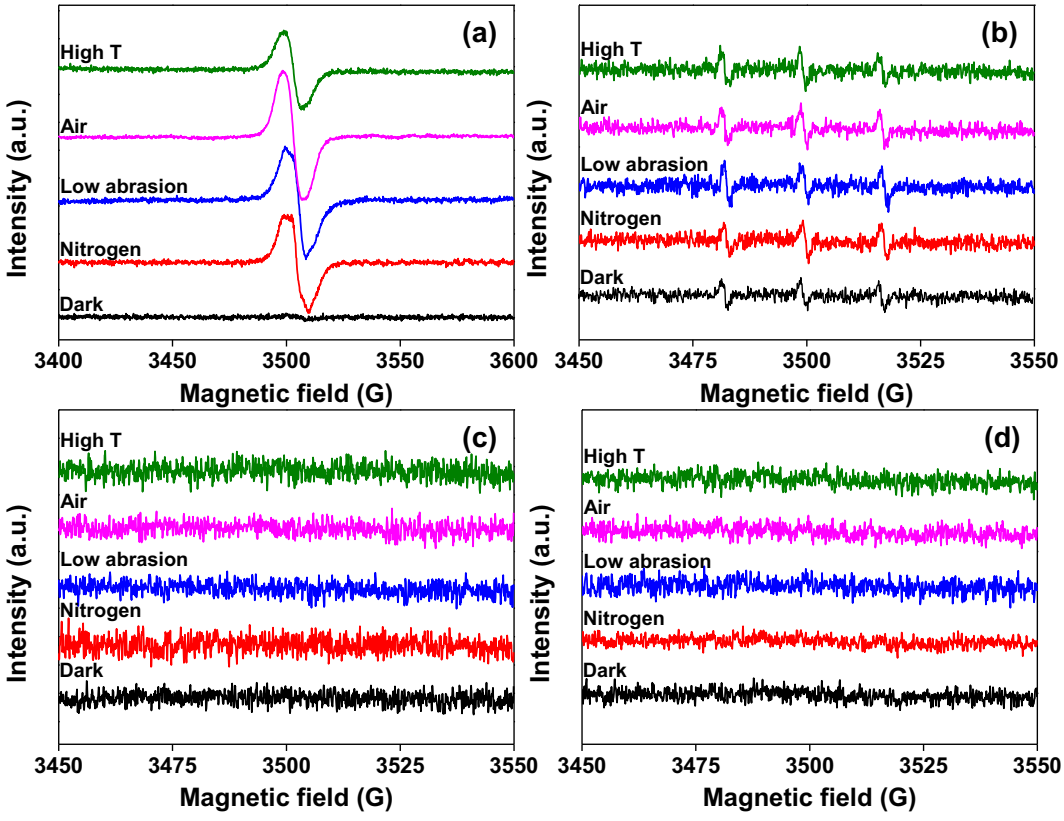

Fig. 5. EPR measurements of reactive species in various photochemical treatments by environmental factors: (a) EPFRs, (b) $^{1}O_2$, (c) OH• and (d) $O_2^{\bullet-}$ (the term "Air" denotes the treatment in high UV with medium oxygen (air), temperature and abrasion; "T" denotes temperature).

Based on these discussions, the ROS-mediated photoaging mechanisms of PS MPs in the presence of various environmental factors were proposed. After being exposed to UV irradiation, the impurities or chromophores in PS firstly absorbed UV energy to generate EPFRs (Singh and Sharma, 2008). Then, EPFRs reacted with dissolved oxygen and formed $^1O_2$ via transfer energy (Zhu et al., 2020). This process may also accompany with the formation of other type of free radicals through a series of reactions (Wang et al., 2022; Zhu et al., 2020). The generated ROS such as $^1O_2$ could attack PS MPs to cause the photooxidation and fragmentation. From these processes, it could be observed that UV energy absorbed by MPs and oxygen content were the two most important factors for controlling photoaging of MPs. Therefore, increasing UV intensity enhanced the photoaging of PS MPs, as shown in Figs. 1 and 2, while a relatively high photoaging in nitrogen-purging condition was likely to be the solution pollution from oxygen in air because the flask was open free of screwing, as discussed in Section 3.1.2. In the same UV irradiation, increasing physical agitation could increase the shearing force and frictional force on MPs, and enhanced the fragmentation. The high temperature treatment resulted in the darker of the solution and reduced the incident light reaching the surface of PS MPs. As a result, the UV energy on the surface of MPs was decreased, inhibiting the photoaging of PS MPs.

3.5. Photoaging behavior of MPs in freshwater

The real photoaging behavior of PS MPs was investigated by incubating in Weihe River surface water samples. FTIR spectra showed that new peak at 1650–1800 cm^{-1} was formed on irradiated PS MPs in freshwater (Fig. S11), similar to the changes in ultrapure water. However, the CI values in freshwater were significantly lower than those in ultrapure water within 15 d of irradiation (Fig. 6a), which suggested the inhibited photooxidation of PS MPs in freshwater. The observation could be further validated by the lower fragmentation of PS MPs in freshwater than that in ultrapure water based on the lower slope value in freshwater (0.02) than in ultrapure water (0.05) seen from the linear variation of d/d_0 versus irradiation time, where d_0 and d denote the average sizes at time 0 and t, respectively (Fig. 6b). This indicated that freshwater environments inhibited the photoaging of PS MPs compared to ultrapure water system. The conclusion could be further reflected by TOC and PL analyses of leachate, where higher TOC and PL intensity occurred in ultrapure water than in freshwater after 15 d of irradiation (Fig. 6c, d).

Presumably, the low photoaging of MPs in freshwater might be related to the water compositions in freshwater (Ding et al., 2022; Wu et al., 2021). Analysis in TOC showed that the content of freshwater was 7.8 mgC/L, compared to nothing in in ultrapure water. In addition, it could be observed that the PL intensity at ~255/450 nm (Ex/Em) were 934 ± 15.3 in leachate of original PS MPs in freshwater, 11.8 times higher than that in leachate from ultrapure water (81 ± 3.7) (Fig. 6d). These results indicated the existence of dissolved organic matters (DOM) in freshwater. As a typical photosensitizer, DOM could generate abundant ROS once being exposed to UV irradiation (Xu et al., 2011), which may enhance the photoaging of PS MPs. However, the presence of DOM in water could shield of PS MPs from UV light, and disturbed their absorption for UV light to induce inhibition effect (Wu et al., 2021). Natural organics matters (fulvic and humic acids) have chromophores that can compete with MPs for photons, and shielded MPs from exposure to UV irradiation. The low photoaging in freshwater of current study indicated that the inhibition effect of DOM was dominant in photoaging of PS MPs. Since the photoaging of MPs in real water was significantly complicated, which was not only dependent on the water constituents and environmental factors, but also correlated to the inherent components such as additives incorporated in MPs, many more efforts should be devoted to comprehensively considering these factors and the contribution in photoaging of MPs to deeply assess the fate and pollution of MPs in aquatic environment.

4. Conclusions

In this study, the effects of various environmental factors including UV, oxygen, temperature and mechanical abrasion on photoaging of PS MPs were investigated in ultrapure water and freshwater. Results showed that UV and mechanical abrasion contributed for the more significant

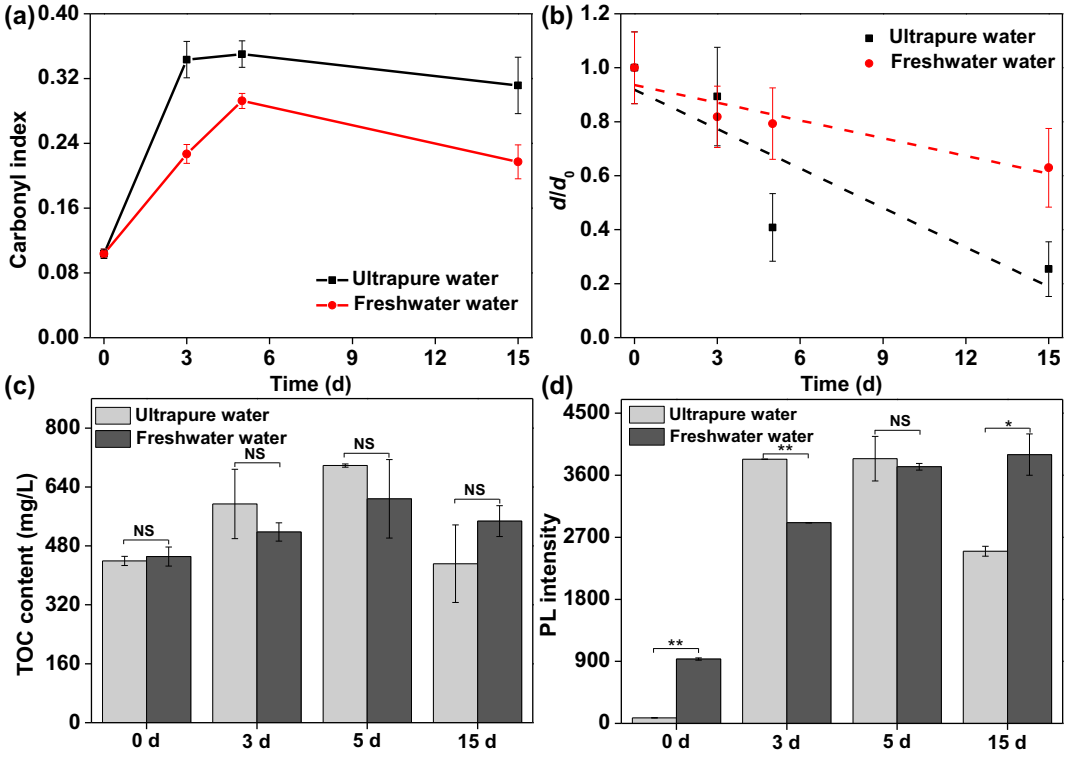

Fig. 6. Photoaging properties of PS MPs in ultrapure (UP) water and freshwater: (a) CI values, (b) particle size, (c) TOC content and (d) PL intensity in leachate (photoaging condition was adopted in high UV, and medium oxygen, temperature and abrasion; NS represents no significance, $^{**}p < 0.01$ and $^{*}p < 0.05$ denote significant difference).

photooxidation and fragmentation of PS MPs among various treatments, suggesting the important role of both factors in the photoaging, as also indicated by TOC and PL analyses. EPR result showed that the photoaging of PS was mainly controlled by ROS ($^1O_2$). Increasing UV intensity could significantly enhanced ROS formation and the subsequent photoaging of PS, highlighting the important role of UV. A higher abrasion could generate stronger shearing and frictional force to enhance the fragmentation. The low effects of oxygen and temperature were caused by multiple factors that worked together on MPs and neutralized the effects of each factors, although many more evidence was needed to validate the assumption. Additionally, the photoaging rate of PS MPs was obviously lower in freshwater than in ultrapure water, mainly ascribed to the disturbance of water constituents (e.g. DOM) on UV absorption by PS MPs in freshwater. Overall, the findings revealed the drivers and limiting factors in the photoaging of MPs in freshwater.

CRediT authorship contribution statement

Jiamin Dai: Writing, Review, Conceptualization.
Peng Liu: Writing, Editing, Conceptualization, Review, Supervision and Funding acquisition.
Chenyang Wang: Investigation.
Huang Li: Formal analysis.
Hong Qiang: Review.
Zeyuan Yang: Formal analysis.
Xuetao Guo: Review, Editing, Supervision and Funding acquisition.
Shixiang Gao: Editing.

Data availability

No data was used for the research described in the article.

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.scitotenv.2022.159845.

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