Adsorption of Copper by Naturally and Artificially Aged Microplastics and Subsequent Release in Simulated Gastrointestinal Fluid

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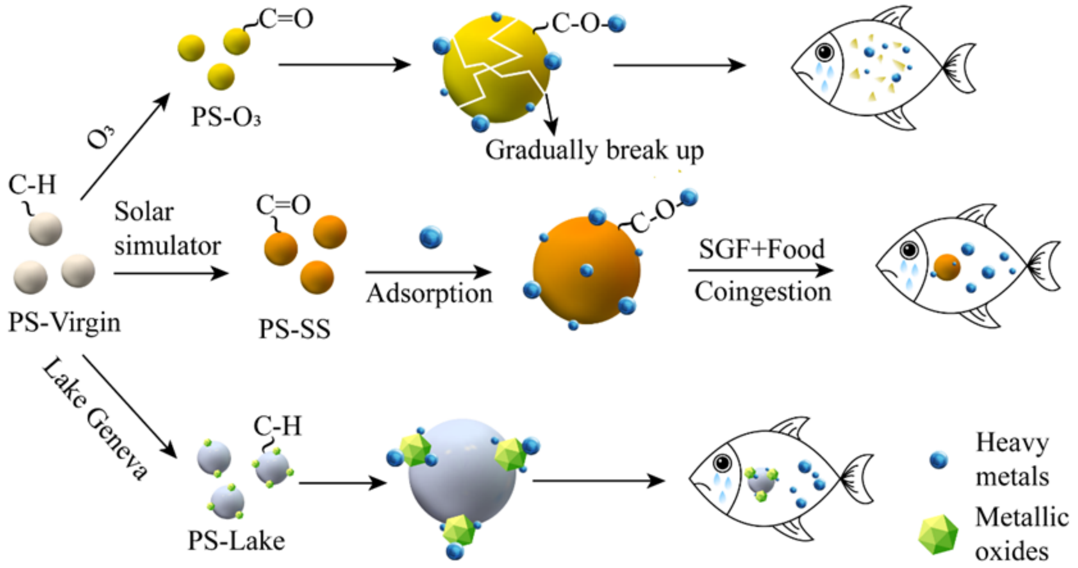

Using in situ and in vitro experiments, this study explores how ageing processes affect the adsorption of copper to microplastics and its bioavailability to aquatic organisms when plastics and food are ingested simultaneously.

ABSTRACT

Microplastics, especially aged microplastics can become vectors of heavy metals from environment to organisms with potential negative effects on food chain. However, a few studies focused on the bioavailability of adsorbed metals and most studies related to aged microplastics used artificial method that cannot entirely reflect actual aging processes. In this study, virgin polystyrene was aged by ozone (PS-O_3), solar simulator (PS-SS) and lake (PS-Lake) to investigate adsorption of Cu by virgin, artificially and naturally aged microplastics and subsequent release in simulated gastrointestinal fluids (SGF). Characterization results show carbonyl was formed in PS-O_3 and PS-SS, and the oxidation degree was PS-O_3> PS-SS> PS-Lake. However, Cu adsorption capacity followed this order PS-Lake (158 μg/g)> PS-SS (117 μg/g)> PS-O_3 (65 μg/g)> PS-Virgin (0). PS-O_3 showed highest Cu adsorption capacity at 0.5 h (71 μg/g), but it dropped dramatically later (10 μg/g, 120 h), because PS-O_3 could break up and the adsorbed Cu released in solutions subsequently. For PS-Lake, precipitation of metallic oxides contributes to the accumulation of Cu. The addition of dissolved organic matter (DOM) could occupy adsorption sites on PS and compete with Cu, but also can attach PS and adsorb Cu due to its rich functional groups. The simultaneous ingestion of microplastics with food suggested that adsorbed Cu is solubilized mostly from aged PS to SGF.

KEYWORDS: Polystyrene; ozone; aging; lake; copper; desorption; gastric fluid

ENVIRONMENTAL SIGNIFICANCE

Microplastics are present in all aquatic environments and undergo various ageing processes. They can act as vectors for organic and inorganic micropollutants such as heavy metals that might affect the metabolism of living organisms. This study aims to gain a better understanding of how ageing processes and the dissolved organic matter influence copper adsorption and its bioavailability to living organisms. The results show that the aging of microplastics in lake water leads to the formation of metallic oxides on their surface contributes to the accumulation of Cu. The *in-vitro* digestion of these particles in presence of food shows that Cu in mainly released in the gastric fluid and could have deleterious effects on aquatic fauna.

INTRODUCTION

Microplastics have drawn widespread attention due to their occurrence in different ecosystems ranging from waters and sediments, to soils and air[1-3]. Microplastics are generally considered to be plastic particles less than 5 mm in diameter, which are formed due to weathering and breakdown of plastics, or cosmetic and personal products.[4-5] Due to the small size and poor degradation rate, microplastics can be mistakenly considered as food and ingested by a wide range of organisms with adverse biological effects.[6-7]

Besides the direct adverse physical effects caused by the microplastics alone, the organic and inorganic additives and adsorbed exogenous contaminants can also constitute a threat to organisms.[8-9] Microplastics can act as vectors of contaminants such as heavy metals from surrounding environment to the bodies of organisms and can disrupt the food chain.[10-11] On the one hand, heavy metals and metalloids are widely incorporated in plastic itself.[12] On the other hand, microplastics can accumulate heavy metals from environment.[13] Concentrations of heavy metals in microplastics are typically on the order of a few ng/g to a few µg/g.[12, 14-15] In natural aquatic environment, dissolved organic matter (DOM) is ubiquitous due to the degradation of plants and animals residuals.[16-17] When microplastics enter the environment, they can interact with DOM, and affects the adsorption of heavy metals because the DOM not only affects the surface charge properties, but could also contains functional groups such as hydroxyl, carboxyl, and amino that can form complexes with heavy metals.[8, 18] Therefore, it is important to investigate the adsorption of heavy metals on microplastics in the presence of DOM. In addition, most present research studied the adsorption of heavy metals by microplastics, but studies related to the bioavailability of adsorbed heavy metals to organisms is comparatively much scarcer.[19-20] Therefore, it is important to investigate the adsorption of heavy metals by microplastics and subsequently release in biological fluids, to assess the contribution of microplastics as a source of heavy metals for aquatic organisms such as fish.

Microplastics released in the environment are susceptible to photo-degradation by ultraviolet radiation, thermal degradation, mechanical abrasion, biodegradation, and oxidation reactions.[21-22] These processes can change the physical and chemical properties of microplastics, including morphology, hydrophobicity, mechanical strength, molecular weight, oxidation degree, etc.[23-24] Many studies suggested that aging processes can increase the adsorption capacity of heavy metals on microplastics because the processes can increase the surface area, hydrophilicity and carbonyl groups of microplastics.[25-26] The aging of microplastics in natural environment is considered to be very slow.[27] Thus, most studies related to aged microplastics carried out the research through artificial aging method, including for instance mechanical stirring, UV and thermal treatments, which are not able to accurately reflect the actual aging processes in natural environment.[21, 23, 28] Therefore, exploration of the transformation of microplastics and their adsorption/release of heavy metals mechanisms in natural aquatic environment is significant to help us to better assess the fate and behavior of microplastics in natural environment.

The aims of the present study are to better assess how the weathering of microplastics affects (*i*) the adsorption of heavy metals and (*ii*) their subsequent release in gastric fluids. To understand these processes, series of experiments were carried out with polystyrene (PS) microplastics. PS was selected as the model plastic, because it is one of the most abundant microplastics, widely used in food and industrial packaging, heat preservation box, and building insulation.[29-31] Copper (Cu) was selected as the target heavy metal, because it is widely found in natural waters, as it originates from antifouling paint and tailings that are not disposed of properly.[32-34] Cu is an essential micronutrient for living organisms only within a concentration range but it can be toxic above the concentration threshold.[35-36] Virgin PS microparticles were artificially aged by ozonation and incubation in a solar simulator. Ozone was used to stimulate atmospheric aging in tropospheric ozone and the solar simulator was used to stimulate the solar radiation on the earth. In addition, PS microparticles were naturally aged in a lake to assess natural weathering in an aquatic environment. The adsorption behavior and mechanisms of Cu on virgin and aged PS were compared to probe into the aging effects on the adsorption of heavy metals by microplastics. The desorption and co-ingestion of PS particles with food in simulated gastric fluids (SGF) were also studied to investigate the release and bioavailabilty of adsorbed Cu in virgin and aged PS.

MATERIALS AND METHODS

Materials. Granulated PS was bought from Carl Roth Gmbh & Co. Micro-PS (PS-

Virgin) was obtained by grinding granulated PS by Retsch MM400 vibro-mill. Ten grams of granulated PS was pre cooled in liquid nitrogen for 10 min to prevent PS from being melted when grinding. The grinding process was set as 50 Hz, 2 min. Cu^{2+} stock solution (1000 mg/L) was purchased from Sigma-Aldrich. Suwannee River natural organic matter (SRNOM, 2R101N) and Upper Mississippi River natural organic matter (UMRNOM, 1R110N) were purchased from the International Humic Substances Society. The SGF simulates the gastrointestinal fluid of fishes (*Oncorhynchus mykiss*), and the preparation of SGF was described in our previous study.[37] The SGF composition is showed in Table S1. The food used in co-ingestion experiments were freeze-dried *Gammarus pulex* (JBL®) obtained from a fish store, and *Lemna minor* which was collected from a pond and dried at 40°C for 3 days. The food was grounded into powder using a porcelain mortar and pestle.

Artificial and in-situ aging methods. Virgin PS was aged by 3 different methods: ozone (PS-O_3), solar simulator (PS-SS) and lake (PS-Lake). For PS-O_3, PS particles were introduced in a glass tube and an ozone generator (Innovatec, CMG 3-5, Germany) was used to create a continuous flow of ozone (3 g/h, 5 h). For PS-SS, a solar simulator with Xe lamp (ATLAS AMETEK, Inc., NEX 1700, USA) was used to simulate the light aging caused by solar radiation of PS-Virgin (irradiance wavelength: 300-800 nm, chamber temperature: 30°C, irradiance power: 1600 W/m^2, irradiance time: 60 d). For PS-Lake, virgin PS was put in nylon mesh bags of 100 μm, the bags were sealed by needle work and food sealing clips. To remove PS-Virgin particles < 100 μm, the nylon mesh bags with PS-Virgin were put in water with rotation overnight. After that, the bags were attached on a rope attached to a floating platform anchored at 570 m of the shore, and the depth of the bags were about 5 cm under the water (46°30’0.819″ N and 6°39’39.007″ E, LéXPLORE, Lake Geneva, Switzerland; https://lexplore.info). The PS particles inside the bag can float on the surface of the lake and were weathered by sunlight.

Characterization methods. The morphology of virgin and aged PS particles was observed by scanning electron microscopy (ZEISS GeminiSEM 300, Germany), equipped with EDX detector (Oxford Inst.) for elements scanning. Contact angle values of ultrapure water were measured using a goniometer (EasyDrop, Krüss, Germany) to measure surface tension between virgin and aged PS particles with water. The functional groups of virgin/aged PS particles were analyzed by ATR-FTIR spectrometer (Perkin Elmer Spectrum Two, USA). The size distribution of virgin and aged PS particles were measured by a particle size analyzer (Beckman Coulter LS 13 320, USA).

Batch adsorption and desorption experiments. To evaluate the impact of the pH on Cu adsorption, the pH value (3.0 – 5.0) of the Cu solution was adjusted by adding 1 mol/L NaOH, because Cu will precipitate above pH of 6 and Cu tend not to be adsorbed under strong acid conditions.[38] The pH was adjusted to optimum value (pH 5.0) in other adsorption experiments. The virgin and aged PS particles (10 g/L) were used for Cu (5 mg/L; Cu solution volume: 100 mL) adsorption and stirred for 3 days in an orbital shaker (160 rpm, room temperature). The concentration of Cu was above environmental concentrations to amplify the short-term Cu adsorption capacity by PS particles and better to observe the Cu adsorption and desorption behavior of PS particles. After adsorption, the PS particles were removed by PTFE filters (0.45 μm). The adsorption experiments over time were performed after adsorption for 0.5, 1, 5, 24, 48, 72, 96, 120 h. To evaluate the impacts of DOM on the Cu adsorption on virgin and aged PS, SRNOM and UMRNOM were dissolved in ultrapure water to prepare DOM stock solution (200 mg/L) and the pH was adjusted to 7.0 using 1 mol/L NaOH. Then the DOM stock solution was diluted appropriately to 0, 10, 50, 100 mg/L for Cu adsorption (Cu: 5 mg/L, pH = 5, 100 mL, 3 d). The concentrations of Cu were measured by ICP-OES (Shimadzu ICPE-9000, Japan). All experimental data was the average of measurements of triplicate samples and the results were expressed as mean ± standard deviation.

After adsorption of Cu, virgin and aged PS particles were collected by filtration using a Büchner funnel (cellulose filter, 0.45 μm). Then the particles were dried in an oven (30°C) prior to desorption in simulated gastric fluid. The desorption of Cu from virgin and aged particles was performed in SGF for 1, 4.5, 20, 44, 68, 92, 116 h (PS: 10 g/L, 100 mL). To assess different co-ingestion scenarios, different ratio of food (food: PS = 2:1, 5:1 and 10:1) and virgin or aged PS particles were added in the SGF (PS: 5 g/L, 50 mL, 24 h). After digestion, the food and PS mixture was removed by filtration (PTFE filter, 0.45 μm), and the digestate sample was diluted 100 times before analysis by ICP-MS/MS (Agilent Technologies LC Infinity II ICP-MS Triple Quad 8900, USA).

RESULTS AND DISCUSSION

Characterization of virgin and aged PS particles. SEM was used to observe the morphology of virgin and aged PS samples, contact angle values of ultrapure water on virgin/aged PS was measured to compare their hydrophobicity and ATR-FTIR was used to analyze changes of functional groups. Figure S1 shows the SEM images of virgin and aged PS particles. From Figure S1 (a), (c), (e), and (g), it can be seen that the virgin and aged PS particles have irregular shape and various size. Figure S1 (b), (d), (f), and (h) show the details of the particle surface. For PS-O_3, the surface is rough and likely due to the erosion caused by ozone. For PS-SS, cracks appeared at the surface, which were generated by the oxidation of ultraviolet. Similar results were observed by Huffer *et al.*, and they explained that polymers such as the polystyrene are particularly susceptible to crack development due to their relatively open structure.[23] For PS-Lake, the surface was smoother than PS particles exposed to other weathering, which may be due to the wash of lake water.

Figure S2 (a) - (d) shows the contact angle values of ultrapure water on virgin and aged PS particles. The water contact angles of PS-Virgin, PS-O_3, PS-SS and PS-Lake were 103.7°, 0°, 0°, and 75.7°, respectively. Generally, the substance is hydrophilic if the water contact angle is 0 - 90°, and the substance is hydrophobic if the water contact angle is > 90°.[39] These results suggest that the aging processes increased the hydrophilicity of virgin PS particles, and PS-O_3 and PS-SS had higher hydrophilicity than PS-Lake. Based on previous studies, it was speculated that hydrophilic contaminants will be adsorbed more tightly on hydrophilic microplastics than hydrophobic contaminants.[40] It was reported that increase of hydrophilic groups in microplastics strengthen their interactions with hydrophilic contaminants in aqueous solutions. Shen *et al.* found that the introduction of surfactants resulted in a higher hydrophilicity of polyethylene (PE), polypropylene (PP) and polymethylmethacrylate (PMMA) particles, and increased the Pb^{2+} adsorption capacity of PE, PP and PMMA.[20] Peng etal. found that the aging of PS and PE particles promoted the accumulation of hydrophilic antibiotics onto aged PS and PE in aquatic environments.[21] Therefore, the aging process could increase the Cu adsorption capacity by PS particles, and the more hydrophilic the particles are, the higher Cu adsorption capacity the particles would have.

Figure S2. (e) shows the color of virgin and aged PS particles. The color of PS-Virgin, PS-O_3, PS-SS, and PS-Lake are white, light yellow, yellow, and grey, respectively. These results further confirm that PS-Virgin apparently changed after the three aging processes. Figure S2. (f) shows the position of virgin and aged PS particles in water. The PS-Virgin particles were floating on the surface of water, the aged PS particles all sank to the bottom of the water, suggesting that the aged PS particles could have a higher affinity for hydrophilic contaminants in water. Figure S3 shows the size distribution of virgin and aged PS, for PS-Solar simulator and PS-Lake, the particles size did not change, but for PS-O_3, the particles size tended to decrease, suggesting the particles could break down to smaller particles.

Figure 1 shows the ATR-FTIR spectra of virgin and aged PS. Compared to PS-

Virgin, there are apparent new peaks in the spectra of PS-O_3. The peak at 1715.51 cm^{-1} represents the carbonyl, implying the C-H in PS-Virgin was oxidized to carbonyl, which is easier to bind with heavy metals.[41-42] For PS-SS, there is also a new peak at 1715.94 cm^{-1} representing the carbonyl, although the carbonyl peak in PS-SS is weaker than that in PS-O_3. However, for PS-Lake, there is not apparent change compared to PS-Virgin. These results suggest that the oxidation degree of three aged PS was PS-O_3 > PS-SS > PS-Lake, which imply that the Cu adsorption capacity by different aged PS particles may follow a similar sequence.

Adsorption of Cu onto virgin/aged PS. To evaluate the effect of different aging processes on the behavior between PS particles and heavy metals, Cu adsorption experiments were conducted at different pH and adsorption time. Figure 2. (a) shows the Cu adsorption capacity of virgin and aged PS at pH = 3 – 5. In natural aquatic environments, the general pH condition varied from 6 to 8, and the general Cu concentration varied from the order of ng/L to μg/L.[43-44] In this study, the Cu concentration was set to 5 mg/L that is higher than that in natural aquatic environments to increase the Cu adsorption capacity of microplastics in a short time. Cu^{2+} will precipitate above pH of 6.2 considering that the Ksp of $Cu(OH)_2$ is 2.2×10^{-20}, and Cu tend to not be adsorbed under strong acid conditions.[45] Therefore, the pH conditions were set to 3-5 in this study. The PS-Virgin had little adsorption capacity towards Cu. For aged PS, the Cu adsorption capacity increased as the pH increased from 3 to 5. The increase of Cu adsorption capacity with pH may be because Cu exists mainly in the form of positively charged Cu^{2+}, Cu^{2+} tended to be adsorbed in higher pH condition. Because carboxylic groups were formed in aged PS, it was possible that carboxylic groups had more negative charges at higher pH.[46] At pH 5, aged PS reached the highest Cu adsorption capacity, with largest Cu adsorption capacity for PS-Lake (158 μg/g), medium Cu adsorption for PS-SS (117 μg/g), and lowest Cu adsorption capacity for PS-O_3 (65 μg/g). These results were surprising because PS-O_3 had the most obvious oxidation degree and PS-Lake seldom had oxidation. There was a significant decrease of Cu adsorption capacity for PS-Lake when pH decreased (pH = 5: 158 μg/g; pH = 4: 61μg/g; pH = 3: 30 μg/g), and the decrease for PS-O_3 and PS-SS were relatively lower, suggesting that the PS-Lake was more sensitive to pH compared to PS-O_3 and PS-SS.

Figure 2. (b) shows the Cu adsorption capacity by virgin and aged PS from 0.5 h – 120 h. PS-Virgin had little Cu adsorption capacity. For PS-SS and PS-Lake, the Cu adsorption capacity increased quickly in the first 24 h and then increasing slowly with the increase of adsorption time. The Cu adsorption capacity of PS-Lake gradually increased after 24 h (103 μg/g at t = 120 h), and that of PS-SS reached adsorption equilibrium after 24 h (70μg/g). The adsorption kinetic of PS-SS and PS-Lake fit the pseudo-second-order kinetic model well (Figure S4， Table S2), implying that the adsorption was more like a chemical adsorption process. Unexpectedly, PS-O_3 showed highest Cu adsorption capacity at 0.5 h (71 μg/g), but the Cu adsorption capacity dropped dramatically with the increase of time (10 μg/g, 120 h). The related adsorption mechanisms is discussed in 3.4.

Figure 3 shows the Cu adsorption capacity onto virgin and aged PS in Cu solution with different concentration of DOM. For PS-Virgin, the Cu adsorption capacity increased a little bit with the addition of DOM. For PS-O_3, although there was fluctuation, the Cu adsorption capacity decreased with the addition of DOM. For PS-Lake, the Cu adsorption capacity shows a decreasing trend with the increase of DOM concentration. For PS-SS, although the Cu adsorption capacity slightly decreased in DOM of 10 and 50 mg/L, it increased significantly in 100 mg/L DOM (SRN: 94 μg/L, UP: 125 μg/L) compared with Cu solution without DOM (75 μg/L). The addition of DOM could occupy the adsorption sites on PS particles and compete with Cu, subsequently decrease the Cu adsorption capacity. However, according to previous studies, DOM also can adsorb on nano- or microplastics and adsorb metals due to its rich functional groups such as carboxyl, carbonyl, acetal, aromatic, and phenolic, which could increase the metals adsorption on plastic particles.[8] In this study, DOM on PS-SS and PS-Virgin played a role of adsorbent for Cu, but DOM on PS-Lake compete with Cu for adsorption sites.

Desorption of Cu from virgin and aged PS. According to above results (3.2), PS particles showed apparent Cu adsorption capacity after aging process. The PS particles can be ingested and accumulated in the bodies of various aquatic and terrestrial organisms, and the adsorbed Cu could be released and enter the food chain. To investigate the release behavior and bioavailability of adsorbed Cu in PS particles, release kinetics and co-ingestion of PS particles with food SGF were investigated.

Figure 4 shows the release of Cu from virgin and aged PS at 1, 4.5, 20, 44, 68, 92, 116 h. For PS-Virgin, there was no detectable Cu release in SGF, because little Cu was adsorbed on PS-Virgin. The release processes were rapid for PS-Lake and PS-O_3 and they reached equilibrium within 1 h and 5 h, respectively. The release of Cu from PS-SS gradually increased, which showed a different trend compared to PS-O_3 and PS-Lake. Figure S5 shows the Cu desorption ratio from aged PS in SGF. The adsorbed Cu in PS-O_3 completely desorbed, while 72% and 58% of adsorbed Cu in PS-SS and PS-Lake, respectively, were desorbed. These results suggests that aged microplastics can serve as vectors of copper and potentially other heavy metals from environment to organisms.

Figure 5 shows the release of Cu in co-ingestion of virgin and aged PS with either vegetal (*Lemna minor*) animal or (*Gammarus pulex*) food in SGF, and the mass ratio of food and PS particles were 2, 5, 10, respectively. For PS-Virgin, there was no obvious change of Cu solubilization after the addition of PS-Virgin comparing to food only, because the Cu adsorption on PS-Virgin was minimal. For PS-O_3, co-ingestion with vegetal food led to a small increase of Cu solubilization but not increase with animal food. The Cu solubilization gap between animal food only and PSO_3 with animal food was tiny, because the release of Cu from PS-O_3 (70 μg/L) was much lower than the Cu released from animal food. For PS-SS and PS-Lake, there was a significant increase of Cu solubilization after addition of PS particles compared to animal or vegetal food only. Table S3 shows the change of dissolved Cu in SGF with the existence of PS particles compared with food only. The Cu originated from PS-SS and PS-Lake increased about 9.17% - 204.63% compared with food only, and the increase was more significant for low food quantity and vegetal food. These results suggest that the PS-SS and PS-Lake lead to greater bioaccessibility of Cu. The release of Cu in co-ingestion scenario was a little lower comparing to the sum of PS particles and food for PS-SS and PS-Lake. These results indicate that Cu solubilized from PS-SS and PS-Lake was partly readsorbed on vegetal and animal food. This is likely because the polysaccharides and proteins in *Lemna minor* and *Gammarus pulex* contain rich functional groups such as carboxyl, amino, hydroxyl and phosphoryl that can bind with metals.[47-48] Overall, the addition of PS can lead to a higher bioaccessibility of Cu although the animal food can act as a complexant for Cu to some extent.

Cu Adsorption and Desorption Mechanisms of virgin/aged PS Generally, the adsorption capacity of heavy metals by PS follows a positive correlation with the aging extent of PS, because the aged PS is more hydrophilic and contains more functional groups such as carboxylic groups that can combine with heavy metals. In this study, the aging extent sequence is PS-O3□ PS-SS□ PS-Lake□ PS-Virgin according to their hydrophilicity and carbonyl content. However, for aged PS, the Cu adsorption capacity sequence is PS-Lake□ PS-SS□ PS-O3. For PS-SS, UV-light was an important aging factor. In addition, UV-light can react with O2 and generate a bit of ozone. The adsorption result is comprehensible for PS-SS, because the aging of PS particles under solar simulator were apparent but weaker than those in ozone. But for PS-O3 and PS-

Lake, the adsorption results are surprising. To investigate the adsorption mechanisms of PS-O3 and PS-Lake, further studies were carried out.

Considering PS-O3 was obtained in an extreme oxidation condition, the particles could break up and decrease the Cu adsorption capacity subsequently. Figure S6 shows the total organic carbon (TOC) released from microplastics of the adsorption system after filtration. The PS-Virgin (0.05 mg/L) and PS-Lake (0.31 mg/L) released little TOC, compared to PS-SS (3 mg/L) and especially PS-O_3 (30 mg/L). In Figure 2 (b), Cu was quickly adsorbed by PS-O_3 in 0.5 h and reached the highest adsorption capacity (71 μg/g), but then Cu released dramatically with the increase of adsorption time. These results suggest that the PS-O_3 has obvious Cu adsorption capacity due to the carbonyl or more carboxylic groups, but the entire particle would be broken in solution and the adsorbed Cu will fall off from the PS-O_3 particles subsequently. These results also can explain the reason that the adsorbed Cu in PS-O_3 released completely in SGF. It has been reported that the C-C bonds in the main chains of the polymers can be cleaved and lead to the fragmentation of the particles under exposure to ozone.[49-50] The research on PS-O_3 helps us understand the fate of microplastics under extreme oxidizing conditions.

In most previous studies, the ultraviolet light, erosion and flush of water are considered the main causes for the aging of microplastics, which lead to the increase of the specific surface area and functional groups of microplastics.[51-53] Consequently, the adsorption capacity of heavy metals by aged microplastics increased obviously compared to virgin microplastics. In this study, the aging duration for PS-Lake was only one month, which was not long enough to cause the apparent change of functional groups in PS. However, it was surprising that PS-Lake had highest Cu adsorption capacity compared to other aged PS. Given that there was no obvious carbonyl peak in ATR-FTIR results of PS-Lake, some other factors came into play. Figure 6 shows the elements distribution of PS-Lake after adsorption of Cu. As we can see, the distribution of Cu was obviously overlapped with that of Si, Al, Mg, Fe and O, which implied that the compounds that contained oxide of Si, Al, Mg, Fe are associated to the adsorption of Cu in PS-Lake. In natural environment, after microplastics enter in water bodies, some abundant elements such as Si, Al, Mg, Fe can gradually precipitate as quartz (SiO_2) and mica ($KAl_2(AlSi_3O_{10})(OH)_2$ (including small quantity of Mg, Fe and other metals), on the surface of microplastics.[54-55] These metallic oxides can subsequently act as adsorbents and accumulate more heavy metals.[56-57] The adsorbed Cu released rapidly and completely in SGF because the metallic oxides on PS-Lake dissolved rapidly in SGF. These results suggest that the heavy metals adsorption behavior of aged microplastics is complex in natural waters, besides the aging effects caused by ultraviolet light, water erosion, the precipitation of metallic oxides can also lead to the accumulation of more heavy metals.

ENVIRONMENTAL IMPLICATION

In this study, virgin microplastics were artificially aged by ozone, solar simulator and were naturally aged in a lake to investigate the fate of microplastics and their interactions with heavy metals. The aged microplastics can combine with Cu, and lead to greater exposure of aquatic organisms like fishes to Cu. In natural aquatic environments, the general Cu concentration varies from the order of ng/L to μg/L, which is lower than the Cu concentration in this study, thus the accumulation of Cu in microplastics may be less.[43] However, the exposure time of microplastics in natural environments is much longer than in this study, which means the aging duration and the accumulation time of Cu is much longer. Moreover, the aging of microplastics will be affected by multiple factors in natural environments due to the long exposure to solar irradiation, mechanical abrasion, mineral sedimentation, etc. and these results could be extrapolated to other heavy metals (e.g. Zn, Cd, Pb, Ni). It can therefore be concluded that the microplastics can act as vectors of heavy metals from environment to organisms and impact their metabolism. An increase in the intake of certain metallic micronutrients such as Cu, Ni and Zn can have deleterious effects. In addition, increased exposure of aquatic organisms to heavy metals such as Cd and Pb can have devastating consequences for ecosystems.

In future studies, it is meaningful to carry out the study of various heavy metals in the order of ng/L to μg/L that is more like a natural aquatic environment. Moreover, it is also meaningful to compare the adsorption and desorption behavior of different metals on common polymers such as polystyrene, polyethylene, polypropylene, polyvinyl chloride but also co-polymers, rubber and biodegradable polymers.

ASSOCIATED CONTENT

Supporting Information: Physical characterization of virgin/aged PS, Pseudo-second-order kinetic model for the adsorption of Cu on PS-SS and PS-Lake, Cu desorption ratio, TOC released from virgin/aged PS, composition of SGF, Change of dissolved Cu in SGF with the existence of PS particles compared with food only.

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FIGURES AND TABLES

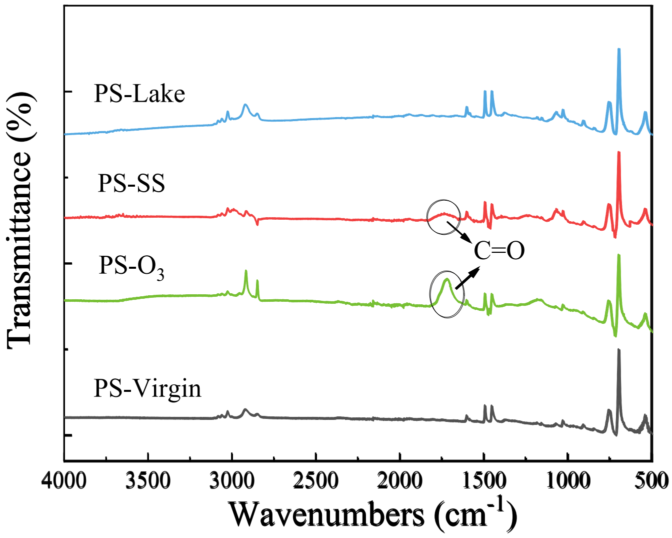

Figure 1. ATR-FTIR spectra of PS-Virgin, PS-O$_3$, PS-SS, PS-Lake.

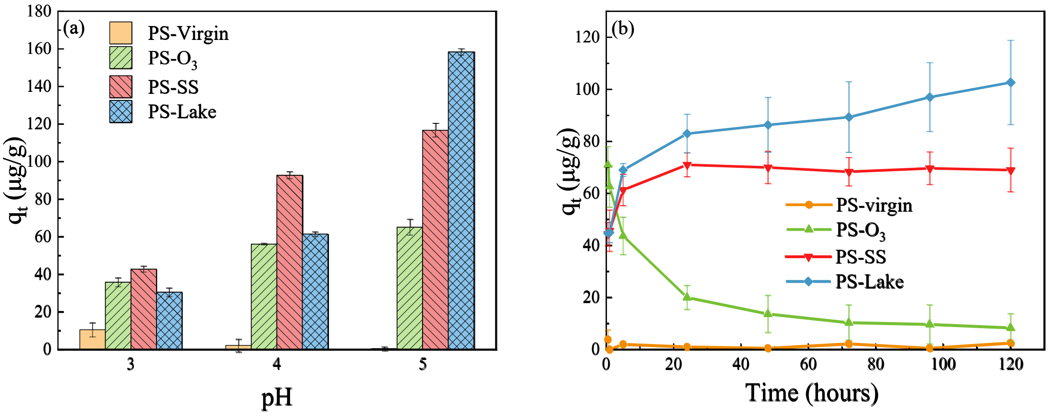

Figure 2. (a) Effect of initial pH on the Cu adsorption capacity of PS-Virgin, PS-O_3, PS-SS, PS-Lake; (b) Adsorption kinetics for the adsorption of Cu onto PS-Virgin, PS-O_3, PS-SS, PS-Lake.

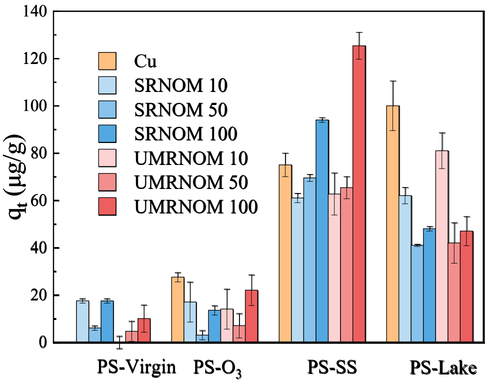

Figure 3. Adsorption capacity of Cu onto PS-Virgin, PS-O$_3$, PS-SS and PS-Lake in Cu solution with DOM (Concentration of DOM: 0, 10, 50, 100 mg/L).

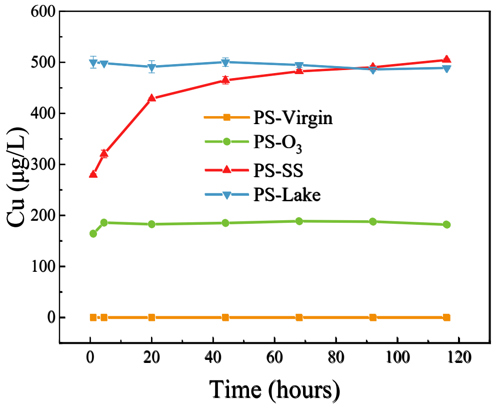

Figure 4. Release kinetics of Cu from PS-Virgin, PS-O$_3$, PS-SS and PS-Lake in SGF.

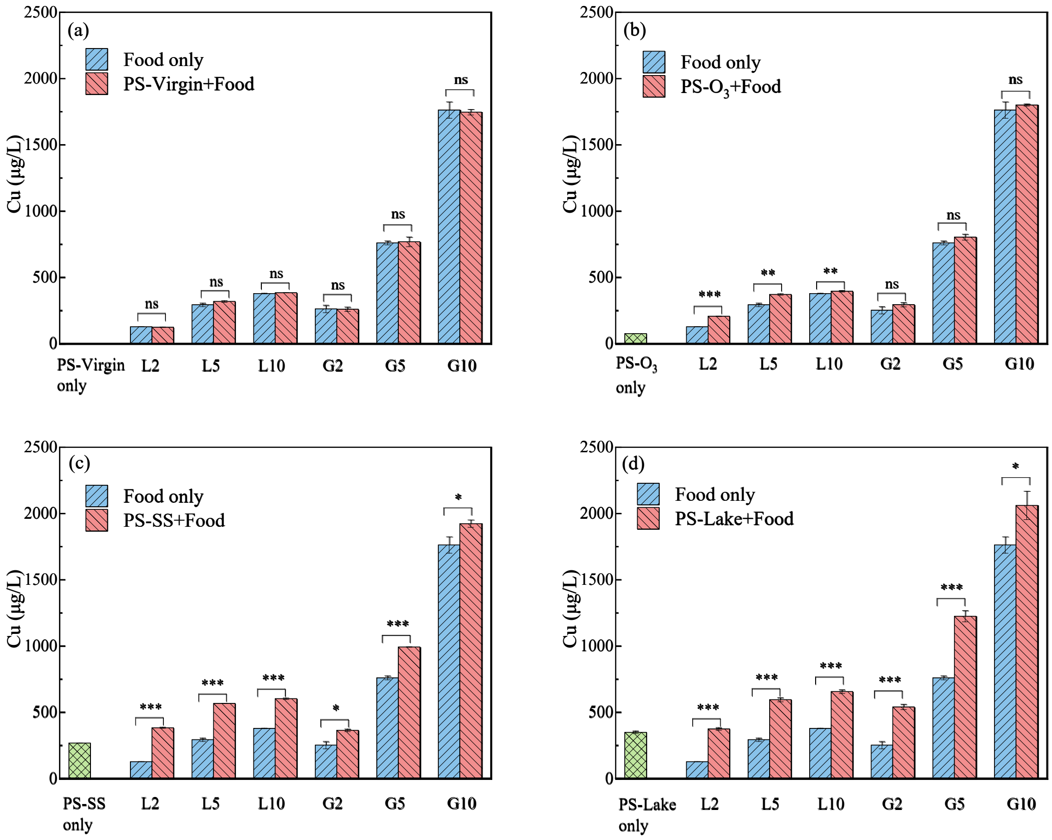

Figure 5. Release of Cu from virgin/aged PS and food in SGF. (a) PS-Virgin, (b) PS-O_3, (c) PS-SS and (d) PS-Lake. (L2, L5 and L10 represent the ratio of *Lemna minor* food to PS are 2:1, 5:1 and 10:1; G2, G5 and G10 represent the ratio of *Gammarus pulex* food to PS are 2:1, 5:1 and 10:1). Statistical analyses with Welch two-samples tests: *, **, and *** represent p value < 0.05, 0.01, and 0.001, respectively.

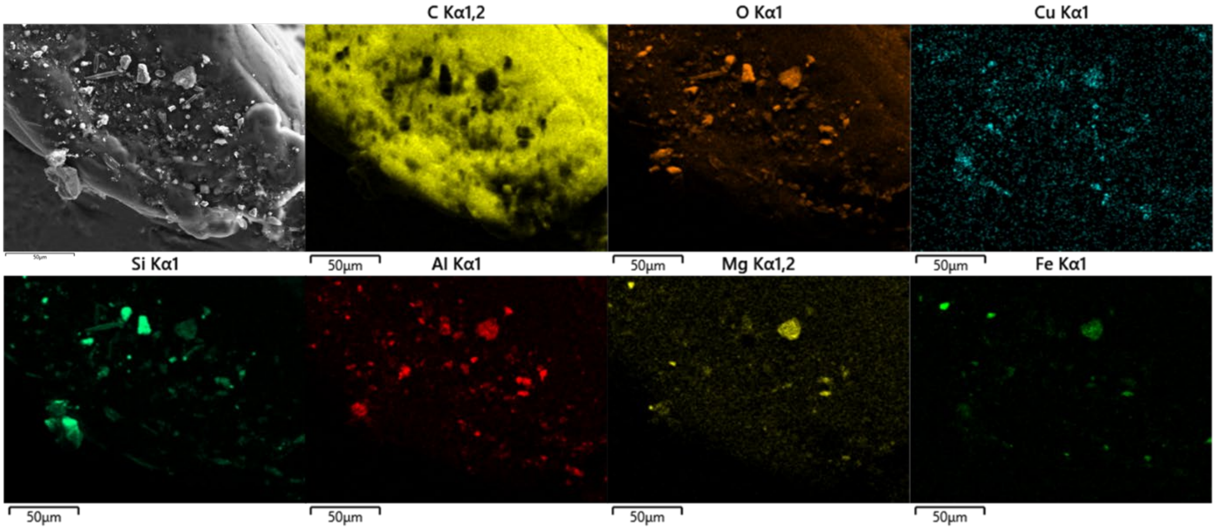

Figure 6 SEM images of PS-Lake and its corresponding EDX mappings for C, O, Cu, Si, Al, Mg and Fe.