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Environmental Microplastics as Vectors of Non-Polar Organic Pollutants in Drinking Water

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Abstract: Microplastics (MPs) in drinking water (DW) raise concerns about their potential impacts on health. Several substances, such as plasticizers and stabilizers, can be leached from plastic polymers following abiotic and biotic denaturation processes. Furthermore, the purification treatment of DW, such as the chlorination process, significantly increases the release of chemical components that are part of the polymer composition. Recently, several studies reported that MPs can adsorb environmental xenobiotics, such as organic molecules and heavy metals, thanks to their surface characteristics acquired in the environment in which they are dispersed. This study aims to evaluate the ability of MPs of different sizes (5 µm and 1 µm) oxidized by UVB exposure to adsorb water-dispersed organic pollutants such as benzo-a-pyrene (BaP). We used Fourier transform infrared spectroscopy and Z-potential measurements to characterize MPs particles after UVB exposure and gas chromatography-mass spectrometry to determine the adsorptive capacity of oxidized MPs. The analytical results obtained from the present study demonstrate that oxidized MPs have a significant capacity to adsorb BaP dispersed in the aqueous environment and to act as a vehicle for apolar organic substances by concentrating them. This study raises an alert on the dual potential risk determined by the consumption of DW in which MPs can concentrate and convey environmental xenobiotics, in addition to deciding adverse effects related to their chemical-physical properties.

Keywords: microplastics; drinking water; organic pollutants

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1. Introduction

Access to safely managed water sources is fundamental for enhancing domestic and food production processes, and it plays a critical role in safeguarding public health. The main goal of the EU's water policy is to ensure that the entire population has access to good-quality water in adequate quantities and that all water bodies are in good condition. The EU Water Framework Directive (2000/60/EC) [1] aims to prevent and decrease water pollution, encourage sustainable water use, and safeguard and improve inland surface waters, transitional waters, coastal waters, and groundwater. Contamination or inappropriate water sanitation treatment to biological agents can lead to the transmission of diseases such

as cholera, diarrhoea, dysentery, hepatitis A, typhoid, and polio. Similarly, inappropriate wastewater management can contaminate DW supply sources [2].

The presence of chemical pollutants in water is not only linked to human activities. In some regions, groundwater may harbour dangerous levels of arsenic and fluoride, which are released naturally from surrounding volcanic rocks. The presence of these harmful substances can pose significant health risks to human health [3]. Other chemical pollutants, such as lead, can be leached from the components of the water network in contact with DW.

In recent years, particular attention has been paid to a new class of persistent pollutants, such as micro- and nanoplastics (MNPs) [4]. Although the effects of this particulate material on the ecosystem are well known, the risks to human health are unclear. The spread of MNPs in water destined for human consumption depends on their chemical and physical characteristics (shape, size, composition), persistence given their low degradation through natural biological processes and the hydrogeological layout of the territory. MNPs environmental routes are generally manifold and often not fully defined. Inland waters are currently considered the main vehicle for transporting these pollutants [5]. Different sources are correlated to the release of MNPs, and it is possible to recognize the earth sources (paints, abrasion of plastic materials such as synthetic turf, city dust), water sources (industrial and civil wastewater, runoff, wear and tear on pipes) and atmospheric sources (transport and deposition of particles by atmospheric agents) [6]. The effectiveness of MNPs removal by water treatment plants is controversial [7,8]. The purification procedures adopted by different systems are heterogeneous and generally do not contemplate the possibility of MNPs removal.

Previous studies demonstrate that conventional water treatment processes such as coagulation/flocculation and sand filtration can remove approximately 58.9–70.5% of MPs [9,10]. Furthermore, when MPs undergo the chlorination process, their chemical structure and hydrophobicity will change, inducing irregularities on their surface, increasing the surface area and consequently modifying their adsorption capacity [11]. Moreover, the large volume of water treated in these systems could contribute to the addition of further particulate matter [12].

Combined sewer systems, the most widespread type of water collection system, simultaneously collect wastewater and rainfall received at street level and convey them to the treatment plant [13]. During severe weather disturbances, water bypasses the system, flowing directly into the receiving water body together with pollutants dispersed in the various environmental matrices. Environmental microplastics, subjected to various aging processes such as microbiological activity and environmental factors, alter their surface structure, decrease in size, and enhance the surface-to-volume ratio. Thanks to their hydrophobicity, MNPs can also act as adsorbent nuclei for organic compounds dispersed in natural waters, making them more bioavailable [14].

The present study aims to evaluate the adsorption capacity of MPs in an aqueous environment towards non-polar organic contaminants, such as BaP. BaP, notoriously included by IARC in group I as a known human carcinogen [15], is an aromatic apolar molecule released by anthropic activity [16] and is one of the main products of the incomplete combustion of organic material such as fuel oil, gas, coal, and wood. BaP is dispersed in the environment at significant concentrations [17] and, being apolar, is usually accumulated on dust particles and in the fats of fauna and flora, finding a high affinity also for the organic fraction of the soil while it does not dissolve well in water.

The DW BaP maximum acceptable concentration in the EU is 0.01 µg/L [18]. Based on the report by ATSDR (1995) [19], the concentration of BaP can range from 0 to 1 µg/L in tap water. On the other hand, water is estimated to account for only 0.1–0.3% of the total BaP ingested [20].

The simultaneous presence of BaP and MPs in DW could further chemical–physical interactions in which plastic particles could represent enrichment nuclei capable of adsorbing and transporting xenobiotics. Water consumption, in which the MPs possibly present have had the opportunity to adsorb environmental xenobiotics, could magnify the adverse effects of pollutants since MPs could concentrate them compared to the quantities present in the environment.

This research questions the capacity of MPs aged by processes triggered by the action of sunlight, when dispersed in water destined for human consumption, to absorb and transport environmental organic pollutants with which they come into contact. Different processes can change the chemical interaction between MPs and environmental organic pollutants. The dimension reduction in particles, such as the change in surface features, could modify the natural binding affinity between two apolar compounds. Moreover, UVB radiation is one of the primary causes of the aging of plastics and alters their structure [21].

For this purpose, we performed several chemical–physical evaluations to determine the changes in MPs characteristics, such as hydrodynamic radius, surface charge, and alteration in surface oxygenated groups, following a photo-ageing process induced by UVB to mimic the environmental process sun inducted. Subsequently, we performed gas chromatography–mass spectrometry (GC–MS) analyses to quantify the concentration of BaP adsorbed by MPs when both were dispersed in water.

2. Materials and Methods

2.1. MP Oxidation

Polystyrene (PS) spheric MPs of two different sizes (1 and 5 µm) were purchased from Cospheric (Santa Barbara, CA 93160, USA) and oxidized by irradiation with 318 nm UVB generated by a lamp (57 V, 20 W G13, Philips, Amsterdam, The Netherlands) for 96 h in an aqueous environment. Specifically, to trigger the oxidative process, 1 mL of MPs (10 mg/mL) was dispersed into a Petri glass dish containing 2 mL of solution performed as an equal volume of H_2O_2 (40%) and Milli-Q water [22], mixed periodically and brought to volume with Milli-Q water. After 96 h, the MPs were centrifuged (12,000 rpm for 15 min), and the resulting precipitate was washed with Milli-Q water and dried by SpeedVac (Jouan RC 10.10 Heated Evaporative Centrifuge Concentrator, Milan, Italy). The MPs obtained were weighed and diluted in Milli-Q water at known concentrations. Ultrasonic devices (Bandelin SONOREX™ SUPER, ultrasonic baths, 35 kHz, Berlin, Germany) were used to resuspend the MPs samples before each use.

2.2. Adsorption BaP-MPs

To promote BaP adsorption in MPsox, 5 mg of MPsox with a size of 1 or 5 µm was dispersed in a glass vial containing 1 mL of a 1 µM BaP aqueous solution and stirred overnight [22].

The 1µM BaP solution was obtained by dissolving 2.52 mg/mL of BaP in acetone to obtain a solution at a concentration of 10 mM that, subsequently, was diluted in Milli-Q water. After incubation, the solution was centrifuged at 12,000 rpm for 15 min to precipitate the MPs from the solution, where the dispersed unabsorbed BaP remains. Subsequently, MPs were resuspended and used for different tests.

The elevated concentration of BaP in water (252 µg/L) utilized in this study effectively simulates the challenging conditions encountered in highly contaminated areas [23].

2.3. Dynamic Light Scattering "DLS"

Dynamic Light Scattering (DLS) analysis was conducted to investigate the hydrodynamic radius and ζ-potential (surface charge) of MPs and BaP-loaded MPs samples. The

analysis was performed utilizing the Zetasizer Instrument, Nano ZS90 Series (Malvern Panalytical, Malvern, UK), equipped with He-Ne laser emitting radiation at a wavelength of 633 nm [21].

MPs were dispersed in deionized water to reach a final concentration of approximately 0.1 mg mL^{-1}, and suspensions were then subjected to 40 kHz sonication for 5 min before each analysis. Measurements were performed at T = 25 °C as a fixed temperature by means of a Peltier thermostatic system, setting the equilibrating time to 120 s; each measurement (of both the hydrodynamic radius and the ζ-potential) consisted of 20 runs, repeated for n times (n = 3, 6, 9).

2.4. Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) investigated and quantified the MPs ageing process. Measurements were performed on a Perkin Elmer Spectrum 65 FTIR equipped with an attenuated total reflectance (ATR) attachment (Waltham, MA, USA). Spectra were generated from 10 stacks of 15 s each and collected in the 4000–500 cm^{-1} range [21]. These spectra allowed us to determine the carbonyl index (CI) [24,25], obtained from the ratio between the absorbance of the carbonyl peak for PS samples, usually calculated at 1730 cm^{-1} and of the reference peak, i.e., the methylene one, usually calculated at 1452 cm^{-1}. FTIR was also used to determine the oxidation index (I_{ox}), a parameter used to confirm the ageing of the samples and quantify it as a function of the oxidized groups [26], calculated through the following formula:

$$I_{ox} = \frac{\int Abs(t)_{C=O}}{\int Abs(t)_{ref}} - \frac{\int Abs(0)_{C=O}}{\int Abs(0)_{ref}}$$

where

$Abs(t)_{C=O}$ absorbance in the region (1615–1840 cm^{-1}) at reaction (ageing) time t;
$Abs(t)_{ref}$ absorbance of reference peaks (1471–1522 cm^{-1}) at reaction (ageing) time t;
$Abs(0)_{C=O}$ absorbance in the region (1615–1840 cm^{-1}) for unmodified polystyrene;
$Abs(0)_{ref}$ absorbance of reference peaks (1471–1522 cm^{-1}) for unmodified polystyrene.

2.5. Gas Chromatography-Mass Spectrometry

Gas chromatography–mass spectrometry was applied to determine the BaP adsorptive capacity of MPs_{ox} and performed as reported by Liu CH et al. [27] with some modifications. Preliminary, the standard calibration was obtained by injecting into an HP5890 series II gas chromatograph coupled to an HP5972 mass spectrometer equipped with an electron impact ionization (IC) source (Agilent, Hong Kong), 5 µL of different BaP standard solutions obtained by diluting a BaP stock solution (1 mM) in cyclohexane at the final concentration: 0.1, 1, 5, and 10 µM.

To assess the adsorption capacity of MPsox at sizes of 1 and 5 µm, we extracted the aqueous supernatant containing BaP, which fails to adsorb to MPsox. This was accomplished by adding 1 mL of cyclohexane and vortexing for 5 min, ensuring a thorough extraction for accurate evaluation. The affinity of BaP, dispersed in water for cyclohexane, allows for the total collection of the compound in the organic phase, which is subsequently injected and analyzed in GC–MS.

GC separation was performed on a DB5MS capillary column (Phenomenex, Torrance, CA, USA, 0.25 mm × 30 m, 0.25 µm film thickness) and using helium gas flow as a carrier, set at 1 mL/min. The injector was set at 350 °C to volatilize the molecule of interest while the column was maintained at an initial temperature of 80 °C. The oven was set at an initial temperature of 80 °C and maintained for 3 min at isotherm conditions, heated at a gradient of 30 °C/min until 240 °C was reached (5.3 min total), further heated at a gradient

of 50 °C/min until 300 °C was reached (1.2 min) and maintained at 300 °C in isotherm conditions for 15 min.

After analyzing the BaP standard, mass spectrometry was performed in SIM (Selected Ion Monitoring) mode, considering the fragments of interest in identifying the BaP standard. After calibration validation, BaP recoveries were calculated using the chosen extraction method. The analyses were performed in triplicate, and the results obtained for each analysis were averaged for each measurement.

2.6. SEM Analyses

This study used field emission scanning electron microscopy (FESEM), installed at DISTAV, University of Genoa, to characterize MPs morphologically. Briefly, MP samples of different sizes and in the naive or oxidized state were vacuum-filtered through a 0.2 µm Whatman polycarbonate filter and air-dried. Subsequently, the samples were coated with graphene by sputtering and visualized using a Tescan Clara FE-SEM UHR axial beam detector, HV, 5 keV, 300 pA.

3. Results

3.1. Fourier Transform Infrared Spectroscopy

MPs FTIR spectra obtained for different MPs sizes, both virgin and oxidized, are reported in Figure 1A,B.

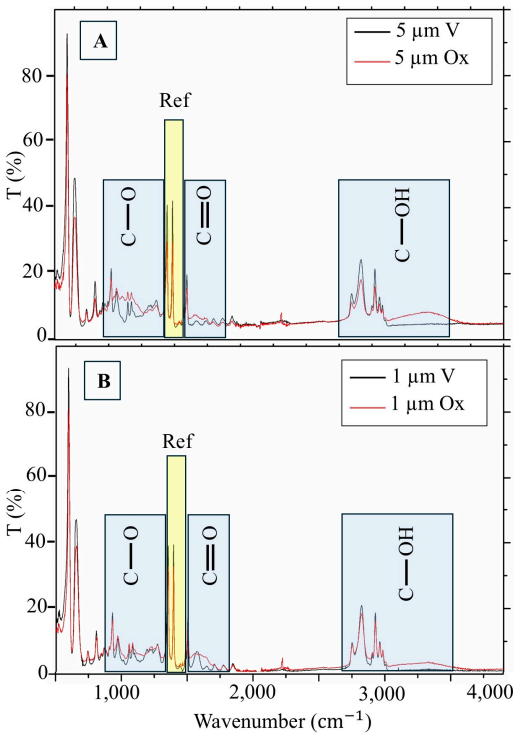

Figure 1. FTIR spectra of MPs range from 4000 to 500 cm^{-1}. MPs before (black line) and after photochemical oxidation (red line) for both sizes 5 µm (**A**) and 1 µm (**B**). Wavenumber ranges for functional groups C=O (blue area) and reference peaks (yellow) are used to calculate oxidation indices I_{ox}.

A broad band centred around 3500 cm^{-1} is observed across all investigated sizes in the oxidized samples. This signal is typical of the stretching vibrations of hydroxyl (C-OH) groups, indicating increased oxygenated functional groups in the oxidized samples. Furthermore, peaks associated with C=O and C-O vibrations appear in the MPs_{ox} within the wavelength ranges of 1650–1750 cm^{-1} and 1100–1350 cm^{-1}, respectively (Figure 1) [25,26].

The analyses highlight the presence of CH_2, with typical signals of their C-H bonds stretching at 2910 cm^{-1}, and aromatic groups, through signals around 3020 cm^{-1}, due to the stretching vibration of their C-H bond, and typical low signals between 1750 and 2100 cm^{-1}, which are affected by the ageing process due to the oxidation of the aromatic group.

As further evidence of photo-oxidation, as the ageing process progressed, the carbonyl index value increased, as reported in Figure 2. The photo-ageing process was further confirmed by the variation of I_{ox} (Table 1), calculated for the aged samples and compared to a standard PS sample.

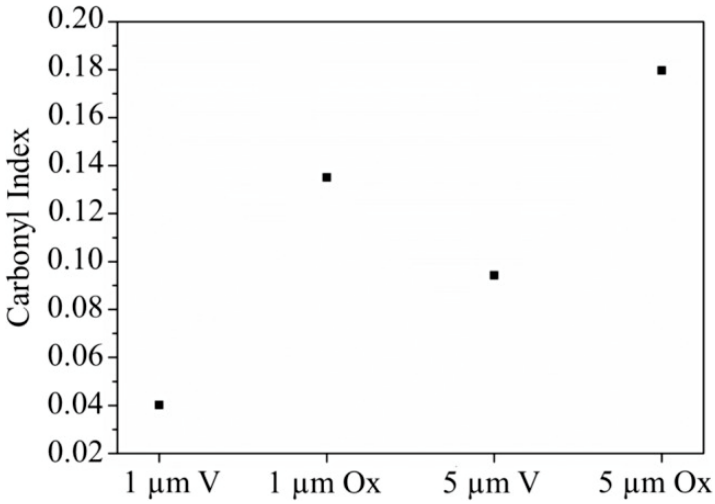

Figure 2. Carbonyl index of MPs samples.

Table 1. I_{ox} value in UVB ageing MPs with different sizes compared to polystyrene (PS).

Sample	I_{ox}
MP_S 1 µm	0.95
MP_S 5 µm	0.90
Standard PS	0.00

3.2. Dynamic Light Scattering

DLS analysis results obtained for 1 and 5 µm MPs, subjected to different conditions, are reported in Table 2.

Table 2. Hydrodynamic radius size (nm) and ζ-potential (mV) results obtained by DLS analysis under different PS conditions (oxidized or virgin) or when oxidized and BaP-enriched.

PS Sample	Condition	BaP	Mean Size (nm ± SD)	Polydispersity Index (nm ± SD)	ζ-Potential (mV ± SD)
1 µm	Virgin	−	1058 ± 100.50	0.50 ± 0.43	−16.0 ± 0.29
	Oxidized	−	855.60 ± 149.60	0.41 ± 0.41	−52.9 ± 1.02
		+	654.50 ± 14.22	0.04 ± 0.01	−42.3 ± 0.54
5 µm	Virgin	−	2980 ± 723.80	0.28 ± 0.08	−40.0 ± 1.27
	Oxidized	−	1604 ± 64.15	0.33 ± 0.05	−40.2 ± 0.70
		+	2770 ± 147.40	0.39 ± 0.05	−49.8 ± 3.01

Moreover, Figure 3 shows the size distribution in the different MPs conditions.

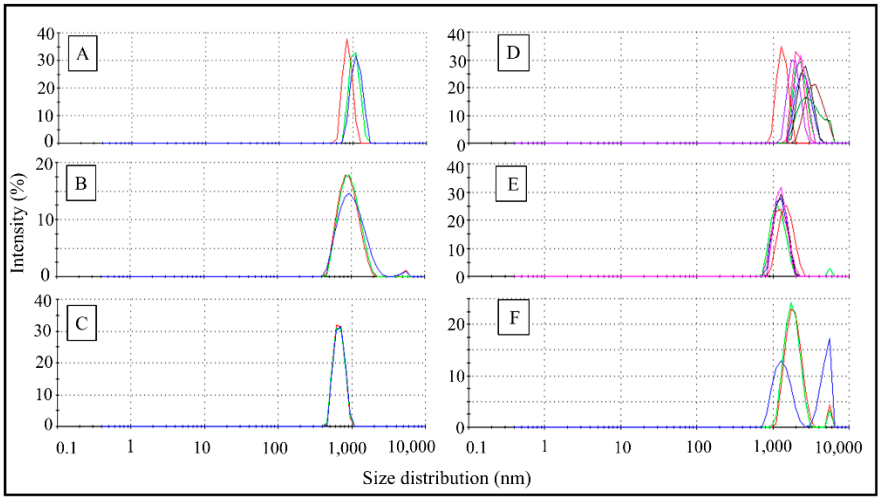

Figure 3. Size distribution obtained by Dynamic Light Scattering of the MPs 1 µm in virgin conditions (**A**), oxidized (**B**), and with adsorbed BaP (**C**), and MPs 5 µm in virgin conditions (**D**), oxidized, (**E**) and with adsorbed BaP (**F**).

Figure 4 shows the ζ-potential distribution of MPs at 1 and 5 µm, respectively.

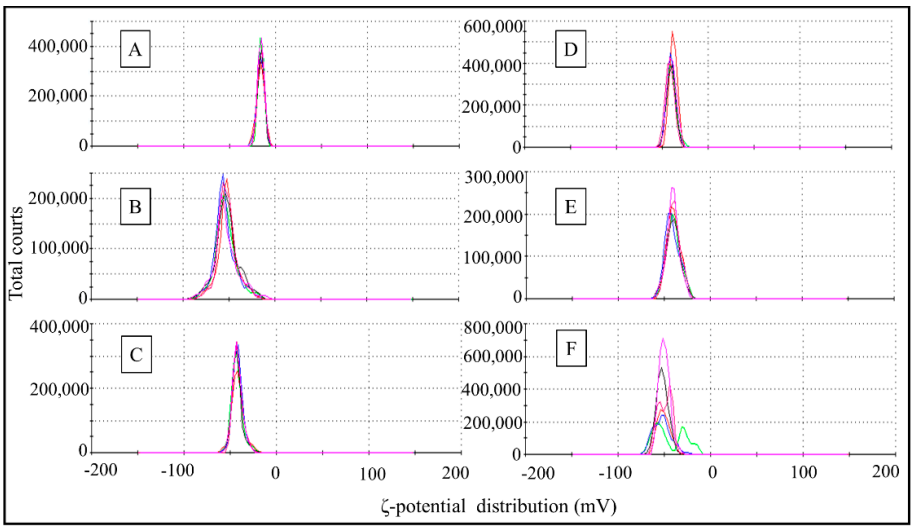

Figure 4. ζ-potential distribution obtained by Dynamic Light Scattering of the MPs 1 µm in virgin conditions (**A**), oxidized (**B**), and with adsorbed BaP (**C**), and MPs 5 µm in virgin conditions (**D**), oxidized (**E**), and with adsorbed BaP (**F**).

DLS characterization highlights surface modifications in PS microparticles triggered by UVB exposition as well as BaP loading. One µm MPs virgin (MPs_V) hydrodynamic radius (Figure 3A) closely corresponds to the nominal size of the commercial PS, also showing a narrow ζ-potential distribution (Figure 4A) around the value of −16.0 mV. The polydispersity index (PdI) related to the hydrodynamic radius measurement is less than 0.5 for all runs, highlighting a low degree of size dispersion for the analyzed samples and indicating that the mean radius distribution overlaps with the average size.

The mean hydrodynamic radius size of MPs_V 5 µm obtained after nine measurements (20 runs per measurement) is 2980 nm with a constant decrease for each subsequent measurement (Figure 3D). The observed effect likely arises from the reduced suspension stability of these particles during the approximately 10 min analysis period. Due to their hydrophobic characteristics, PS particles exhibit significant instability in water suspensions.

Depending on the material's density, this instability manifests as agglomeration, settling, or floating. Notably, this issue becomes more pronounced with larger particles.

The results highlight how oxidation by UVB exposition decreases the mean hydrodynamic radius. Additionally, the smaller hydrodynamic radius of the BaP-loaded particles appears to be due to their distinct behaviour in an aqueous environment. These effects are further illustrated in the diagram reported in Figure 3, where the hydrodynamic radius of the 1 µm MPs_v vs. MPs_{ox} (Figure 3A,B) and the 5 µm MPs_v vs. MPs_{ox} are compared (Figure 3D,E). The size distribution peaks show changes as a function of the condition of the sample (virgin and oxidized), thus suggesting that a modification in the surface behaviour induced by UVB exposure likely occurred. These results are confirmed by microphotographic images obtained by FESEM (Figures 5 and 6).

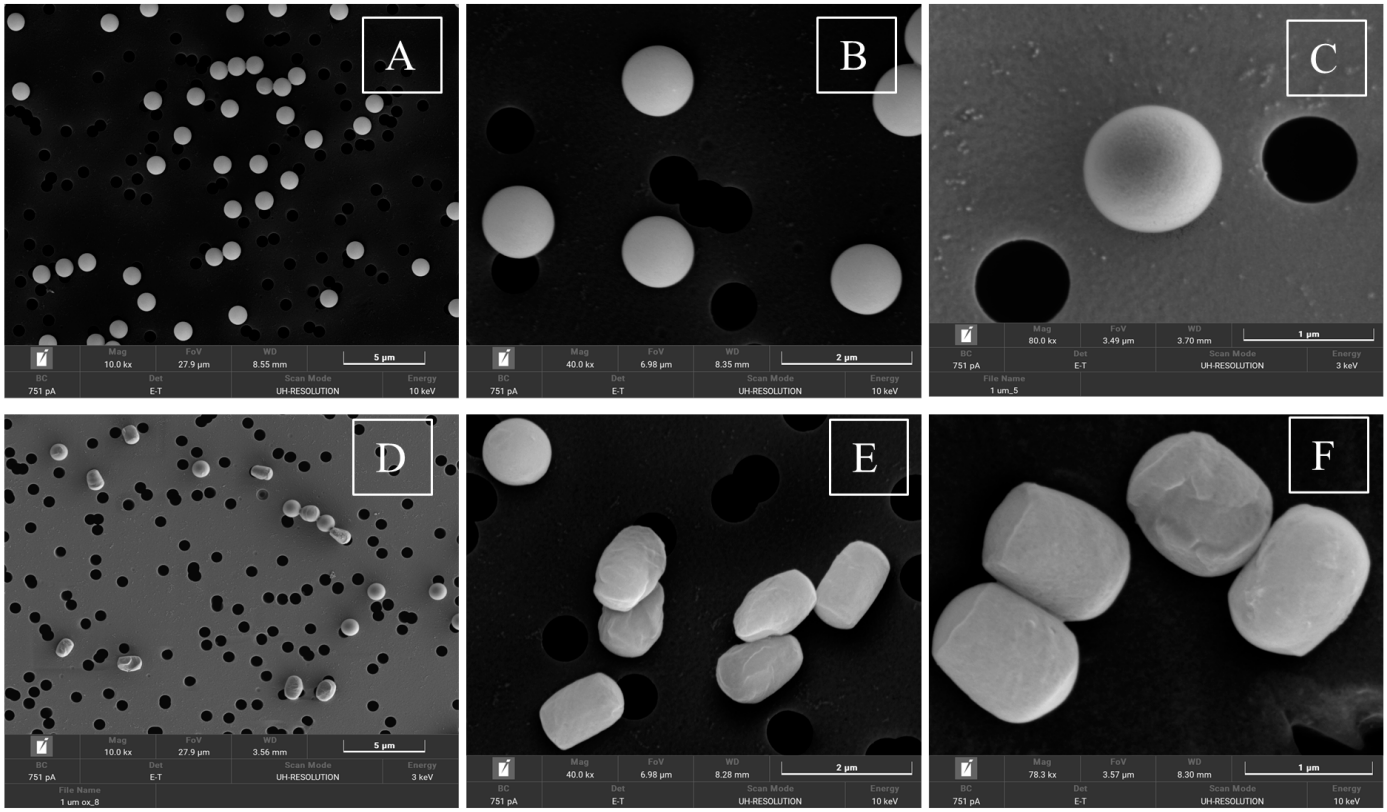

Figure 5. FESEM microphotographs of the MPs 1 µm referred to virgin as (**A**–**C**) and oxidized as (**D**–**F**), respectively.

The fragmentation mechanism caused by UVB oxidation can involve several types of bond cleavage. The overall process eventually leads to a variation in the surface charge distribution and, as a result, alters how the polymers interact with the medium in which they are dispersed.

The oxidation process plays a crucial role in impacting the surface charge, particularly in the 1 µm MPS samples (Table 2). Specifically, as reported in Figure 4A,B, the ζ potential of the 1 µm MPs samples increases following the oxidation processes (MPs_v -16.0 ± 0.29 mV vs. MPs_{ox} -52.9 ± 1.02 mV). Furthermore, for the MPs_{ox}, a more heterogeneous distribution is evident, probably due to the different surface conditions.

In contrast, analysis of the 5 µm MPs (Figure 4D,E) reveals that while the mean value of the ζ potential remained relatively constant, a broader distribution was observed. Also, the surface adsorption of BaP influenced the samples response, resulting in a slight change in the measured values, but the effect still needs to be clarified precisely.

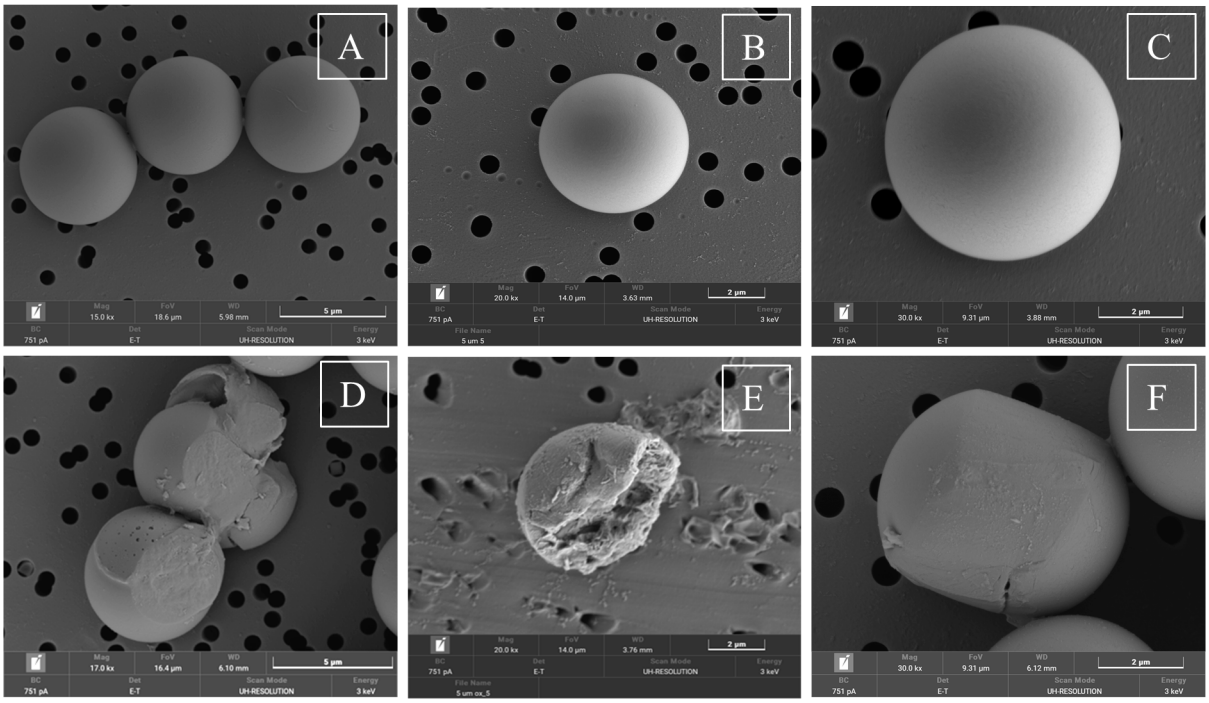

Figure 6. FESEM microphotographs of the MPs 5 µm referred to virgin as (**A**–**C**) and oxidized as (**D**–**F**), respectively.

3.3. Gas Chromatography-Mass Spectrometry

The GC–MS analysis demonstrates that the recovery of non-absorbed BaP in water varies between 1 µm and 5 µm microplastics (MPs). These variances are likely attributed to the differing surface-to-volume ratios, which are especially impactful for the smaller particles. In fact, the recovery rate of non-absorbed BaP in the water with 1 µm MPs was just 21.2%, whereas it soared to 66.7% for the 5 µm MPs when compared to the initial concentration. Consequently, this leads to the conclusion that 1 µm MPs adsorb a substantial 78.80% of BaP, while only 33.30% is captured by the 5 µm MPs. This underscores the critical role of particle size in the interaction with pollutants.

Referring to the initial concentration of BaP (1 µM) in water, we can effectively determine the amount of BaP adsorbed by each milligram of MPs. Our experiment exposed 5 mg of microplastics to 1 mL of a 1 µM BaP solution. Given that BaP has a molar mass of 252.32 g/mol, we determined that 1 mg of 1 µm MPs adsorbs 40 ng of BaP, while 1 mg of 5 µm MPs adsorbs 17 ng of BaP (refer to Table 3).

Table 3. Non-absorbed BaP recovery by CG–MS analysis.

Size MPs_{ox}	Non Absorbed BaP (%)	Absorbed BaP (ng/mg MP_S)
1 µm	21.2	40
5 µm	66.7	17

4. Discussion

This study tests the ability of MPs, which are scattered in water and have undergone a photo-oxidation process attributable to the action of UVB emitted by the sun, to adsorb hydrophobic environmental pollutants such as BaP.

Water supply for human consumption comes mainly from surface and underground resources. Concentrations of BaP in DW are typically very low, with the primary source often being the coating of the water distribution pipes rather than the raw water source.

Water can contact various pollutants such as polycyclic aromatic hydrocarbons or MPs during flow. The chemical–physical properties of MPs and organic compounds, such as BaP, dictate their chemical interactions, primarily governed by electrostatic bonds [28].

When released into the environment, MPs undergo continuous degradation processes, mainly triggered by the sun's direct action [29]. This involves an increase in the surface/volume ratio and an alteration of surface electrostatic charges. Exposure to UVB causes significant alterations in the structure of irradiated MPs.

Analyses conducted with DLS show different behaviour in the size distribution as well as in the surface charge, both being more pronounced for 1-micron MPs. These findings support the conclusion that the photo-oxidation process causes structural alterations in the particles, which result from degradation processes induced by UVB irradiation, dependent on the MPs' size, contributing to the loss of the surface polymer layer and particle integrity.

The continuous reduction in size causes MPs to disperse more quickly in different environmental matrices. Their low density causes meteorological processes, such as rainfall, to collect and convey these ubiquitous pollutants towards hydrographic basins [5].

Particular attention should be paid to the anthropic context in which the higher concentrations of BaP and MPs increase the probability of interactions between the two pollutants.

Sewerage systems and rainwater collection usually use a mixed system in which urban and rainwater wastewater is conveyed. In this environmental context, ubiquitous pollutants such as MPs and non-polar organic pollutants generated by combustion can easily establish chemical interactions.

Under the conditions reported in our study, it is demonstrated that MPs present different adsorbent capacities, attributable to their size when they have undergone a photo-aging process similar to that determined by sunlight in the aquatic environment according to the scheme reported by Hu et al. [25]. The data obtained confirm that the process triggered by the exposure of MPs to UVB has determined an alteration of the chemical–physical structure of the particles. Specifically, the most remarkable effects were highlighted in the 1 μm particles that have significantly altered their surface charges and hydrodynamic radius. This could be related to tiny particles being more susceptible to degradation processes than large MPS. A higher surface area to volume ratio means that a larger portion of the particle body is available for electrochemical interactions involving the polymeric structure of the plastic material. As a result, smaller particles have a greater adsorption capacity for the same mass than larger particles.

The carbonyl index and I_{ox} confirm the oxidation process occurring for both sizes of MPs. However, the analysis performed at the ζ-potential highlights a substantial difference in charges only for the 1 μm MPs. This difference is related to the presence of BaP, which influences the ζ-potential by moderating the surface charge.

Interestingly, the GC–MS analysis of the water contaminated with BaP and recovered after the dispersion of the MPs confirmed the adsorbent capacity of these PS particles for the molecule tested. Chemical adsorption plays a crucial role in the interaction between microplastics and BaP molecules, often facilitated by π–π interactions or hydrogen bonding between the polar groups on their surfaces [30].

Noteworthy, Yin et al. [31] report that oxidized MPs that adsorb non-polar compounds, such as benzo(a)anthracene, can limit their environmental degradation. This occurs due to competition between oxygen-containing functional groups and the light-shielding effects provided by oxidized microplastics.

These interactions, widely studied in the ecotoxicological context, have been evaluated mainly by in vivo studies to clarify the toxicological potential of the MPs-xenobiotic binomial but rarely clarify the adsorbent capacity of the plastic polymer. On the other hand, previous study indicates that the sorption capacity of microplastics (MPs) for non-polar

compounds like phenanthrene and nitrobenzene varies with particle size. Specifically, Wang [32] found that nanoscale particles exhibit lower adsorption capacity due to aggregation, which reduces their effective surface area. Our findings reveal an inverse correlation between MP size and adsorption capacity, although we did not use nanoplastics in our study. MP pollution is a difficult issue to solve regarding the supply and treatment of water intended for human consumption. Removing this particulate matter is not fully guaranteed by the various physical and chemical treatments used to improve surface water quality. Presumably, in some cases, such as chlorination, the number of micro and nano plastics dispersed in the water system could increase. In fact, thanks to its high oxidizing capacity, chlorine could modify and weaken the structure of the polymer with which it reacts, triggering, in many cases, further fragmentation.

In this context, it has been demonstrated that the 1 μm MPs, when oxidized and dispersed in water, adsorb more than double the BaP compared to 5 μm MPs. Additionally, as Cheng et al. [28] demonstrated, the bond between PS and BaP is dictated by hydrophobic interactions, which is much more evident in a polar medium such as water.

5. Conclusions

The results underscore the urgent need to focus on the significant health risks associated with microplastics, as they have the ability to adsorb harmful non-polar environmental pollutants in drinking water. This issue warrants immediate action to safeguard human health and ensure the safety of our water supply. The variation in MPox size seems to be the key factor that significantly impacts the adsorption of BaP when dispersed in water. Understanding this relationship is essential to elucidate the adsorption processes. This study, considering only oxidized MPs at two different sizes, mimics the natural process that plastics undergo when released into the aquatic environment. Furthermore, it confirms that the chemical–physical alterations induced by exposure to light modify the structure of MPs and ensure the bond with BaP.

Due to sudden climate changes, water is an indispensable element and increasingly difficult to find. Currently, greater attention must be paid not only to water's poor availability but also to its quality.

MPs, as well as other emerging pollutants, pose significant concerns regarding the risks associated with ingesting these particles and their potential impact on public health. Moreover, current water sanitation methods are ineffective at removing MPs. To improve these conditions, advancements in filtration systems that successfully eliminate microparticles are necessary. Additionally, further research is needed to assess the potential toxicological risks of MPs and their capacity to adsorb and release environmental xenobiotics within the human body.

Author Contributions: Conceptualization, S.L.M.; methodology S.L.M. and F.D., validation, M.B., G.D. and S.A.; formal analysis, M.B., S.A., A.S. and L.G.; data curation, S.L.M.; writing—original draft preparation, S.L.M. and L.F.; writing—review and editing, S.L.M. and F.D.; supervision, S.L.M.; project administration, S.L.M. All authors have read and agreed to the published version of the manuscript.

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References

1. EU Water Framework Directive (2000/60/EC). Available online: https://eur-lex.europa.eu/legal-content/IT/TXT/?uri=CELEX:32000L0060 (accessed on 9 November 2024).
2. GBD 2016 Diarrhoeal Disease Collaborators. Estimates of the global, regional, and national morbidity, mortality, and aetiologies of diarrhoea in 195 countries: A systematic analysis for the Global Burden of Disease Study 2016. *Lancet Infect. Dis.* **2018**, *18*, 1211–1228. [CrossRef] [PubMed]
3. WHO. *Guidelines for Drinking-Water Quality Incorporating the 1st Addendum*, 4th ed.; World Health Organisation: Geneva, Switzerland, 2017; ISBN 978-92-4-154995-0.
4. Sun, X.; Zhu, Y.; An, L.; Liu, Y.; Zhuang, Y.; Wang, Y.; Sun, M.; Xu, Q. Microplastic Transportation in a Typical Drinking Water Supply: From Raw Water to Household Water. *Water* **2024**, *16*, 1567. [CrossRef]
5. Kye, H.; Kim, J.; Ju, S.; Lee, J.; Lim, C.; Yoon, Y. Microplastics in water systems: A review of their environmental impacts and potential hazards. *Heliyon* **2023**, *9*, e14359. [CrossRef]
6. Ali, M.U.; Lin, S.; Yousaf, B.; Abbas, Q.; Munir, M.A.M.; Ali, M.U.; Rasihd, A.; Zheng, C.; Kuang, X.; Wong, M.H. Environmental emission, fate and transformation of microplastics in biotic and abiotic compartments: Global status, recent advances and future perspectives. *Sci. Total Environ.* **2021**, *791*, 148422. [CrossRef] [PubMed]
7. Tang, N.; Liu, X.; Xing, W. Microplastics in wastewater treatment plants of Wuhan, Central China: Abundance, removal, and potential source in household wastewater. *Sci. Total Environ.* **2020**, *745*, 141026. [CrossRef]
8. Elkhatib, D.; Oyanedel-Craver, V.A. Critical review of extraction and identification methods of microplastics in wastewater and drinking water. *Environ. Sci. Technol.* **2020**, *54*, 7037–7049. [CrossRef]
9. Murphy, F.; Ewins, C.; Carbonnier, F.; Quinn, B. Wastewater Treatment Works (WwTW) as a Source of Microplastics in the Aquatic Environment. *Environ. Sci. Technol.* **2016**, *50*, 5800–5808. [CrossRef]
10. Pivokonsky, M.; Cermakova, L.; Novotna, K.; Peer, P.; Cajthaml, T.; Janda, V. Occurrence of microplastics in raw and treated drinking water. *Sci. Total Environ.* **2018**, *643*, 1644–1651. [CrossRef]
11. Syranidou, E.; Nicolas, K. Interactions of microplastics, antibiotics and antibiotic resistant genes within WWTPs. *Sci. Total Environ.* **2022**, *804*, 150141. [CrossRef]
12. Talukdar, A.; Kundu, P.; Bhattacharya, S.; Dutta, N. Microplastic contamination in wastewater: Sources, distribution, detection and remediation through physical and chemical-biological methods. *Sci. Total Environ.* **2024**, *916*, 170254. [CrossRef]
13. Foundation for Water Research (FWR). *Microplastic in the Freshwater Environment*; FWR: Marlow, UK, 2017.
14. Costigan, E.; Collins, A.; Hatinoglu, D.M.; Bhagat, K.; MacRae, J.; Perreault, F.; Apul, O. Adsorption of organic pollutants by microplastics: Overview of a dissonant literature. *J. Hazard. Mater. Adv.* **2022**, *6*, 100091. [CrossRef]
15. IARC Monographs on the Identification of Carcinogenic Hazards to Human. Available online: https://monographs.iarc.who.int/list-of-classifications (accessed on 29 November 2024).
16. U.S. Centers for Disease Control Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Polyaromatic Hydrocarbons (PAHs)*; ATSDR: Atlanta, GA, USA, 1995.
17. Bukowska, B.; Mokra, K.; Michałowicz, J. Benzo[a]pyrene-Environmental Occurrence, Human Exposure, and Mechanisms of Toxicity. *Int. J. Mol. Sci.* **2022**, *23*, 6348. [CrossRef] [PubMed]
18. Directive (EU) 2020/2184. Available online: https://eur-lex.europa.eu/eli/dir/2020/2184/oj (accessed on 20 November 2024).
19. ATSDR. *Toxicological Profile for Polycyclic Aromatic Hydrocarbons*; Agency for Toxic Substances and Disease Registry, Public Health Service, U.S. Department of Health and Human Services: Atlanta, Georgia, 1995. Available online: www.atsdr.cdc.gov/toxprofiles/tp69.pdf (accessed on 20 November 2024).
20. WHO. *Guidelines for Drinking Water Quality*; World Health Organisation: Geneva, Switzerland, 1984; Volume 3, pp. 183–189.
21. La Maestra, S.; Benvenuti, M.; Alberti, S.; Ferrea, L.; D'Agostini, F. UVB-Aged Microplastics and Cellular Damage: An in Vitro Study. *Arch. Environ. Contam. Toxicol.* **2024**, *87*, 48–57. [CrossRef]
22. Batel, A.; Linti, F.; Scherer, M.; Erdinger, L.; Braunbeck, T. Transfer of benzo[a]pyrene from microplastics to Artemia nauplii and further to zebrafish via a trophic food web experiment: CYP1A induction and visual tracking of persistent organic pollutants. *Environ. Toxicol. Chem.* **2016**, *35*, 1656–1666. [CrossRef] [PubMed]
23. Minnesota Pollution Control Agency. *2017 Health Risk Limits Nominations*; Minnesota Pollution Control Agency: St. Paul, MN, USA, 2017.
24. Zhang, Y.; Peng, Y.; Peng, C.; Wang, P.; Lu, Y.; He, X.; Wang, L. Comparison of detection methods of microplastics in landfill mineralized refuse and selection of degradation degree indexes. *Environ. Sci. Technol.* **2021**, *55*, 13802–13811. [CrossRef]
25. Hu, J.; Lim, F.Y.; Hu, J. Characteristics and behaviors of microplastics undergoing photoageing and advanced oxidation processes (AOPs) initiated ageing. *Water Res.* **2023**, *232*, 119628. [CrossRef]
26. Vicente, J.S.; Gejo, J.L.; Rothenbacher, S.; Sarojiniamma, S.; Gogritchiani, E.; Wörner, M.; Kasperb, G.; Braun, A.M. Oxidation of PS aerosols by VUV-Photolysis and/or Ozone. *Photochem. Photobiol. Sci.* **2009**, *8*, 944–952. [CrossRef] [PubMed]

27. Liu, C.H.; Shin, Y.N.; Chou, Y.C.; Peng, G.J.; Shen, Y.R.; Lin, N.C.; Chang, S.H.; Kao, Y.M.; Tseng, S.H.; Wang, D.Y. Determination and validation of polycyclic aromatic hydrocarbons (PAH4) in katsuobushi, plant-based food supplements, and cocoa bean shells using GC-MS/MS. *J. Food Drug Anal.* **2024**, *32*, 472–481. [CrossRef]
28. Cheng, S.; Ye, Z.; Wang, X.; Lian, C.; Shang, Y.; Liu, H. The effects of adsorbed benzo(a)pyrene on dynamic behavior of polystyrene nanoplastics through phospholipid membrane: A molecular simulation study. *Colloids Surf. B Biointerfaces* **2023**, *224*, 113211. [CrossRef]
29. Wilkinson, J.; Hooda, P.S.; Barker, J.; Barton, S.; Swinden, J. Occurrence, fate and transformation of emerging contaminants in water: An overarching review of the field. *Environ. Pollut.* **2017**, *231*, 954–970. [CrossRef]
30. Zhu, Z.; Sun, L.; Qin, Q.; Sun, Y.; Yang, S.; Wang, J.; Yang, Y.; Gao, G.; Xue, Y. The Adsorption Process and Mechanism of Benzo[a]pyrene in Agricultural Soil Mediated by Microplastics. *Toxics* **2024**, *12*, 922. [CrossRef] [PubMed]
31. Yin, L.; Zhang, S.; Liu, B.; Zheng, Q.; Wang, Z.; Qu, R. Investigation of the photolysis process of benzo(a)anthracene (BaA) on polyvinyl chloride (PVC) and polystyrene (PS) microplastics: Plastics aging effect, transformation products and toxicity assessment. *Sci. Total Environ.* **2024**, *929*, 172394. [CrossRef] [PubMed]
32. Wang, J.; Liu, X.; Liu, G.; Zhang, Z.; Wu, H.; Cui, B.; Bai, J.; Zhang, W. Size effect of polystyrene microplastics on sorption of phenanthrene and nitrobenzene. *Ecotoxicol. Environ. Saf.* **2019**, *173*, 331–338. [CrossRef] [PubMed]

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