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Spatial–Temporal and Risk Assessment of Microplastics in the Surface Water of the Qinhuai River during Different Rainfall Seasons in Nanjing City, China

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Abstract: Microplastics (MPs) are increasingly becoming recognized as worldwide environmental contaminants, exerting a substantial impact on the safety of city rivers. This study explored the temporal variance in MPs in different rainfall seasons, including spring, plum, and autumn rains. The Qinhuai River has large spatial fluctuations in MPs at six sampling sites, with an average concentration of 466.62 ± 153.69 items/L, and higher MP abundance was found downstream of spring rain and upstream of autumn rain. Among the different rainfall seasons, the variations in microplastics at various sampling sites were more stable in the plum rain season, with an average concentration of 473.67 ± 105.17 items/L, while the concentrations of TP and TN in the plum rain season were higher than those in other rain seasons. Transparent MPs had the highest abundance at many sampling sites in all seasons, and large-sized MPs (270–5000 μm) occurred more in the autumn rain season. PVC was more prevalent in autumn, but PET decreased in the plum rain season. Interestingly, more fibers, PET, and large-sized MPs were found in the autumn rain. The index of hazard scores of plastic polymers (*H*) revealed that the studied river was at a severe pollution level (IV), which was highly influenced by PVC and PC. In addition, the pollution load index (*PLI*) value in different rain seasons indicated slight pollution (I). At the same time, it was higher in autumn rains than in other seasons due to the higher variance in MPs. Therefore, the ecological risk of microplastics in the Qinhuai River should be seriously considered, along with seasonal variance and the PVC and PC polymers. Our research is expected to provide valuable assistance in improving the management of urban rivers.

Keywords: urban rivers; seasonal variation; microplastics; spatial abundance; risk assessment

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1. Introduction

Microplastics (MPs), which are particles smaller than 5 mm, are universally recognized as a worldwide pollutant. These minuscule plastic granules are ubiquitous and can be discovered in various environmental settings, including the atmosphere [1], ocean [2], and rivers [3], threatening both water quality and human health [4]. Microplastics, because of their small size and extensive surface area, can absorb hazardous substances, leading to increased toxicological harm, including the presence of polycyclic aromatic hydrocarbons (PAHs) [5], heavy metals [6], and antibiotic resistance genes [7]. Consequently, scientists globally are progressively focusing on understanding the existence and fate of microplastics.

Researching the origins and pathways of microplastics in the environment is crucial for gaining a profound comprehension of how microplastics are distributed in the biosphere [8]. Prior studies have established the existence of microplastics in river environments. Among developed countries, the Patterson River had an MP abundance of 9 ± 15 items/L [9],

and the Portugal River had an average of 8–71 n/m^3 [10]. Developing countries showed a higher MP abundance than developed countries. In China, the levels of microplastics in freshwater resources were measured at 9.30 × 10^5 items/m^3 during dry seasons and 4.97 × 10^5 items/m^3 during wet seasons in the lower Yellow River [11]. Concurrently, it was discovered that the mean concentrations of microplastics in the surface water of the Pearl River were 1.99 × 10^4 items/m^3 in the urban area and 8.90 × 10^3 items/m^3 in the estuary [12]. Urban rivers have been sufficiently investigated in southern and northern China, while urban rivers in the eastern region have not received enough attention. Moreover, urban rivers act as conduits for the entry of microplastics from urban sources into the surrounding ecosystems [13]. Approximately 80% of ocean plastic pollution originates from inland regions [14]. The occurrence of microplastics is frequently attributed to a combination of dense populations and industrial activities near urban rivers [15], which include the discharge of wastewater treatment plants (WWTPs) and seepage from large-scale manufacturing facilities [16]. These sources serve as possible channels for releasing primary microplastics into the ecosystem. Therefore, the examination and assessment of microplastics in urban rivers can help researchers understand the transport and transformation processes of microplastics (MPs) in urban freshwater ecosystems.

The abundance of microplastics exhibits significant variation in many studies, which is mainly attributed to disparities in seasonality, environmental factors, and analytical methodologies [17]. Multiple seasonal studies have shown that there are fluctuations in microplastics in the surface water of river catchments [18], river basins [19], and river sediments [20]. Simultaneously, previous studies on microplastics have typically used only one sampling assessment and have been limited to a specific period [21]. Further investigation should focus on the temporal or seasonal fluctuations in and the environmental dynamics of microplastics in rivers. Rivers have the potential to be sources and repositories of microplastics, acting as recipients in the smaller drainage areas during periods of low precipitation and as origins for the main river during periods of high precipitation [22,23]. Hence, it is imperative to take into account temporal fluctuations when assessing the indicative prevalence of microplastics in regions with significant seasonal precipitation [24].

It is imperative to assess the ecological and environmental dangers associated with microplastics by considering their physical and chemical properties. Nevertheless, there remains a deficiency of standardized assessment techniques. Scientists have investigated the potential for microplastic pollution in different parts of the environment using different assessment models. For instance, Le et al. (2023) [25] employed the risk ratings of plastic polymers, as suggested by Lithner et al. (2011) [26], to construct a compilation encompassing various types of microplastic polymers and a pollution load index (PLI) measure. Additionally, Kabir et al. [27] employed the ecological risk index approach established by Tomlinson et al. [28] to evaluate the occurrence of microplastics in the sediments of Japanese rivers on a small scale and high risks of MP pollution in the rivers were found at all sampling sites. Therefore, risk assessment approaches for microplastic pollution should be extended to include urban river systems as well.

In this study, the concentration and properties of microplastics were investigated in the Qinhuai River in eastern China. The aim of this investigation was to examine the spatial–temporal variability in microplastics with consideration given to seasonal fluctuations in May, July, and September, which represent three rainfall seasons: spring rain, plum rain, and autumn rain. An investigation was conducted to examine the presence of microplastic contamination in terms of its quantity, color, size, shape, and polymers in different reaches of the river. An evaluation was also conducted to determine the potential ecological hazards associated with microplastics using various indices. This study not only provides new information on the seasonal variation of MP characteristics in the urban river but also provides a comprehensive risk assessment of MPs. The investigations offer suggestions and data for the scholars and government officials involved in the relevant field.

2. Materials and Methods

2.1. Study Area

The Qinhuai River, referred to as the QH River, is the primary river in Nanjing City, Jiangsu Province, spanning around 110 km. The studied area is situated between 31°40′ and 32°10′ N latitudes and 118°35′ and 119°0′ E longitudes, including various stream sections for upstream (WC and YQ), midstream (JD and QW) and downstream (JZ and SC) in Figure 1. The central section of the river in Nanjing is traversed by two main tributaries, namely the QH River in the northwest and the New QH River in the west. The upper reaches of the region are predominantly characterized by industrial zones, but the middle reaches are characterized by the presence of parks and a thriving tourism industry. The lower sections, on the other hand, consist mainly of residential districts. The topography of the studied river exhibits a south-to-north gradient, characterized by steep inclines and alluvial fans at the higher elevations and gradual slopes in the middle and lower regions. The sampling strategy primarily aims to acquire samples from varied areas in the water environment, which includes six sampling sites with three parallel samples.

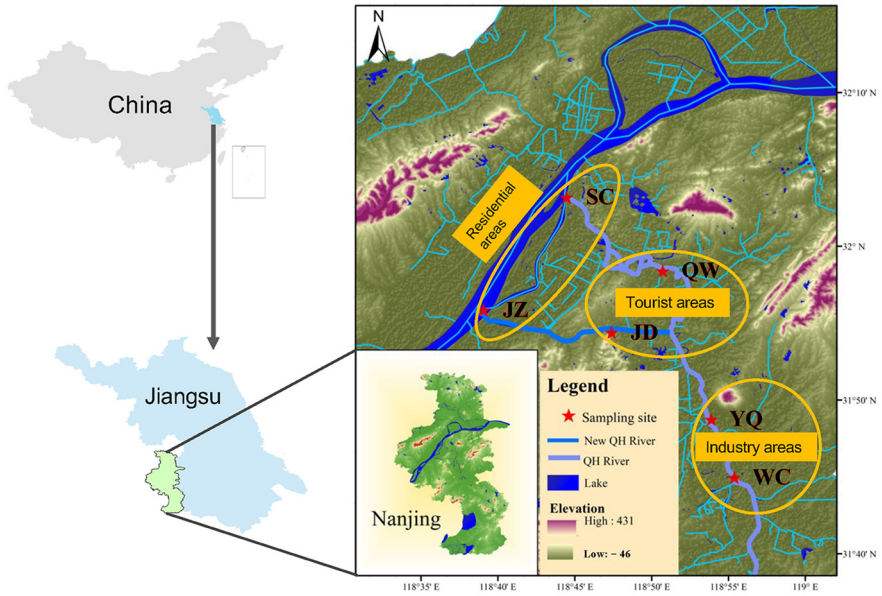


Figure 1. The geographical coordinates and sampling locations along the Qinhuai River (upper reaches: YQ, WC; middle reaches: JD, QW; lower reaches: JZ, SC).

With a distinct subtropical monsoon climate, Nanjing exhibits pronounced rainfall patterns. To analyze and identify the characteristics of microplastics (MPs) in correlation with rainfall seasons, more obvious monsoon climates were selected, with 54 water samples in May, July, and September representing spring rain, plum rain, and autumn rain, respectively. Table S1 provides comprehensive data regarding the six sampling sites.

2.2. Collection of Microplastic Samples

Surface water was collected in the Qinhuai River by using a bucket of containers, with three parallel samples in a stainless steel tester. The sampling equipment underwent cleaning and rinsing with filtered tap water before being passed through a sequence of gravity filters. Stainless steel mesh screens with specified mesh sizes (micrometer of 5000, 270, 38, 150, and 75) were utilized to capture different-sized MPs. The sampling method is mainly referred to the previous study [29]. The sample receptacles underwent a triple cleaning process to ensure the transfer of all specimens onto the stainless steel mesh screen. The mesh screen components underwent three rounds of thorough cleaning before being transferred to a 500 mL beaker for subsequent laboratory analysis. These beakers were

encased in aluminum foil and subjected to a 12-hour drying period at a temperature of 90 °C.

The wet peroxide oxidation (WPO) method was utilized for the degradation of organic substances, with the Fenton reagent serving as a crucial catalyst in the accelerated oxidation process facilitated by H_2O_2. The beakers were filled with a volume ranging from 20 to 50 mL of a solution containing 30.00% H_2O_2 and an equal volume of a solution containing 0.05 M $FeSO_4$. The concoction was, thereafter, heated to 60 °C with continuous agitation. Following the WPO method, the samples underwent density separation and were treated with 100 mL of a solution containing $ZnCl_2$ before being left undisturbed overnight. The liquid portion was passed through a nitrocellulose grid membrane by vacuum filtration method, then the membrane was examined on a sterile dehydrated glass Petri dish.

2.3. Identification of Microplastic

A stereo microscope and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) were employed to detect the microplastics. Initially, a stereo microscope (Leica, EZ4 56, Wetzlar, Germany) was utilized to ascertain the potential microplastics with diameters of 38–5000 µm. In addition, several colors (blue, red, yellow, translucent, white, green, black) and shapes (granules, fragments, films, fibers) were selected. The representative microparticles were utilized by ATR-FTIR spectroscopy (Nigoleto, IS 40, USA) to identify the kinds of polymers.

2.4. Quality Control

A clean specimen was acquired using pristine mesh screens positioned on the ground. Before the collection in a 500 mL beaker, the three steel mesh screens were washed thrice with Milli-Q water. Prior to conducting background sampling, random samples were gathered to assess both the existence of microplastic pollution and the cleanliness level of the steel mesh screens at the sampling sites. To optimize the sampling method's effectiveness, the recovery experiment was performed thrice using polystyrene (PS) microspheres (manufactured by Huzheng Nano Technology Co., Ltd., Shanghai, China) with sizes of 100 µm and 74 µm. The recovery rates for the 100 µm and 74 µm PS microspheres are 93.24% and 95.32%, respectively, suggesting that the trial maintained high-quality control standards. Furthermore, precautionary measures were enacted to avoid any potential contamination from occurring. This included washing all ingredients and glassware thrice with ultrapure water before usage. Additionally, every step was conducted under an aluminum foil cover, and cotton lab coats were worn throughout the procedure.

2.5. Microplastic Risk Assessment Method

At present, there is no established and universally applicable model for evaluating the environmental risks linked to microplastic pollution. Consequently, scientists have devised a resilient risk assessment framework that can be applied to many contaminants to comprehensively comprehend and estimate the ecological hazards of microplastic contamination [30,31]. Two approaches were used in this work to examine the pollutant features of microplastics in river surface water to determine the potential ecological concerns associated with them. An index quantifying the microplastic polymers' chemical toxicity to the ecological environment was established using the initial methodology. Table S2 displays the hazard scores for the pertinent polymers [26]. The formula that was applied was as follows:

$$H = \sum P_n \times S_n \quad (1)$$

H represents the risk indicator associated with the polymers found within the microplastics, the hazard score (S_n) of the plastic polymers, and the percentage of microplastic polymer types (P_n) retrieved at each sampling location, which is revealed in Table S2.

Employing the pollutant loading index as an important index PLI, the second method evaluated the ecological risk [28,30]. In this study, the environmental threat presented by

microplastic contamination in the Qinhuai River was assessed using microplastic concentration rather than the pollutant load.

$$CF_i = \frac{C_i}{C_{0i}} \tag{2}$$

$$PLI = \sqrt{CF_i} \tag{3}$$

$$PLI_{zone} = \sqrt[n]{PL_1 PL_2 \cdots PL_n} \tag{4}$$

The parameter CF_i is derived by dividing the concentration (C_i) of microplastics at individual sampling sites by the lowest level of microplastic concentration (C_{0i}). C_i denotes the concentration of microplastic observed at each sampling location. The accuracy and precision of these data rely on the experimental methods and instruments used. C_{0i} is a defined value that is symbolized in the study by the lowest concentration of microplastics present in each sampling site [32]. The microplastic ecological risk index is evaluated using the PLI, which represents the load index of microplastics on the basis of MP concentration. A list of MP criteria, presented in Table S3, defines the level of risk associated with polymers.

2.6. Statistical Analysis

Water quality of chemical oxygen Demand (COD), total nitrogen (TN), and total phosphorus (TP) parameters were analyzed according to standard methods (Chinese, N.E.P.A). The concentration of the gathered microplastics (MPs) was determined by dividing the total number of MPs by the sample volume, with the data reported in terms of mean standard error in items per liter (items/L) units. ANOVA comparison was used to compare the datasets, and the significance level was set to 0.05. Statistical analyses and graphical representations were performed using SPSS (2023) and Origin (2024b) software for all analyses.

3. Result and Discussion

3.1. MP Abundance in the Spatial Distribution

The average microplastic abundance of three rain seasons was calculated in Figure 2. The findings revealed that the abundance of microplastics ranged from 121 to 719 items/L, with a sum mean of 466.62 ± 153.69 items/L. In terms of microplastic abundance, the QH River exhibited a lesser quantity compared to Korea (the Nakdong River, 1970 ± 62 items/L) [33] and England (the Thames River, 44.3–510 items/L) [34]. However, it had a higher abundance than most city rivers in China, such as the Pearl River (8.73–53.25 items/L) [12], Poyang River (5–34 items/L) [35], Wei River (4.67–12.3 items/L) [36], and Han River (2.32–8.41 items/L) [37]. The findings suggest that the extent of microplastic (MP) pollution in the Qinhuai River is comparatively moderate compared to other origins, implying that the Qinhuai River could significantly contribute MPs to the Yangtze River.

The upstream area gathers some industrial enterprises, while tourist scenic spots and residential areas were located in the midstream and downstream, respectively. When analyzing industry effluents, it was found that effluents from textile wet processing industries contained over 1000 times more microfibers than those from municipal wastewater treatment plants (WWTP) [38]. Due to the rapid development of the tourism industry, tourists are identified as a major source of anthropogenic plastic input [39]. Simultaneously, the various residential activities that generate municipal wastewater are equally important when considering the sources of microplastics in aquatic systems [40]. Figure 2 also demonstrates the fluctuation pattern of various sampling locations, indicating that the average concentration of microplastics initially decreases, then increases, and finally decreases downstream. As for different reaches, upper reaches showed a significantly higher MPs abundance (518 ± 155.78 items/L) than other reaches ($p < 0.05$), while more volatility was found in midstream (440.67 ± 255.13 items/L) sampling sites. The regional distribution of microplastic abundance exhibited a peak concentration in the WC region, with a value of 543.3 ± 155.78 items/L upstream. This region is characterized by significant anthropogenic

activity and the accumulation of external pollution. The surrounding environment exerted more MP pressure on the location upstream, which is located in a place with lots of roads, restaurants, businesses, and regular human activities, such as waste disposal and domestic sewage, resulting in significant microplastic contamination [41,42]. As for the downstream, the MP concentration was 441.17 ± 148.80 items/L, with 452.67 items/L and 429.33 items/L in JZ and SC. A non-obvious gap of average MP abundance is detected downstream, which indicates lighter MP pollution in the urban river near the estuary of the Yangtze River.

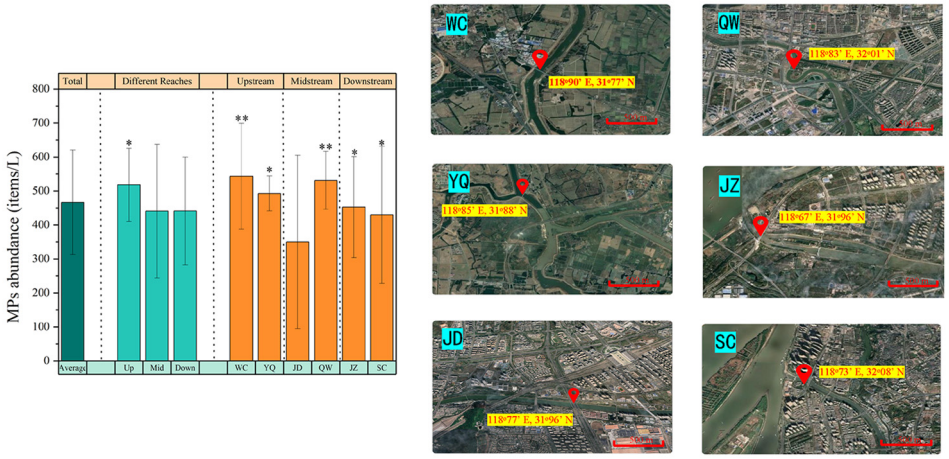


Figure 2. Overall spatial distribution of microplastic abundance in the Qinhuai River. (Significant differences between the different groups are shown by * ($p < 0.05$) and ** ($p < 0.01$)).

3.2. MP Abundance in Seasonal Variation

In order to obtain comprehensive information on microplastics in rivers, it was more reliable to study the different seasons of MPs in fresh rivers and lakes. The MP abundance of different reaches in the same rain seasons was revealed in Figure 3A. In the spring rain, the abundance ranged from 304 ± 39.85 to approximately 662 ± 40.15 items/L, with an average abundance of 513.17 ± 140.22 items/L. Compared to the research conducted in spring rain, the downstream showed a relatively higher MP abundance. With the increasing warming temperatures and human activities, humans have become the main source of microplastic pollution in the downstream, which is near residential areas. The same phenomenon was found in site QW, where scenic tours are conducted; tourists left behind rubbish, including bottles of mineral water and food packaging bags, which also made the MP content increase, which was consistent with the previous study in the same sampling sites of Qinhuai River [43]. In Autumn rain, the abundance ranged from 121 ± 44.53~719 ± 37.73 items/L, with an average abundance of 413 ± 208.51 items/L. MP abundance upstream was higher than in other sampling sites, which may be due to the atmospheric transmission and precipitation. For plum rain, the increase in rainfall relatively diluted the level of microplastic contamination. Thus, insignificant differences in concentration were found among sampling sites. The highest MP concentration in JD is mainly attributed to its actual geographical factors, close to wastewater treatment plants (WWTPs), which resulted in a significant amount of microplastics discharging in the surface water of urban rivers.

Three rain seasons showed spatial variance of MP abundance in six sampling sites (Figure 3B). The variance of MP abundance ranged from 309 to approximately 625 items/L in plum rain, which was relatively stable than that in spring and autumn rain, with the range of 304~662 and 121~719 items/L. With the increasing rainfall in the plum rain season, microplastics were vulnerable to moving with high-velocity water flow, and microplastics in the surface water were hardly concentrated in the fixed sites, which caused relatively stable variances of MPs in different sampling sites. High-velocity water flow would facilitate microplastics to migrate during the rainy season, and the concentrations of microplastics

progressively decrease as the water volume increases [31]. Conversely, previous studies have demonstrated that precipitation can cause sediment resuspension and facilitate the transport of microplastics from land into river systems. The phenomenon may contribute to the increased abundance of microplastics in surface water during the rainy season [23,44]. Overall, the average abundance of microplastics was moderate in plum rain, indicating that rainfall would not increase the MP exposure risk in the Qinhuai River.

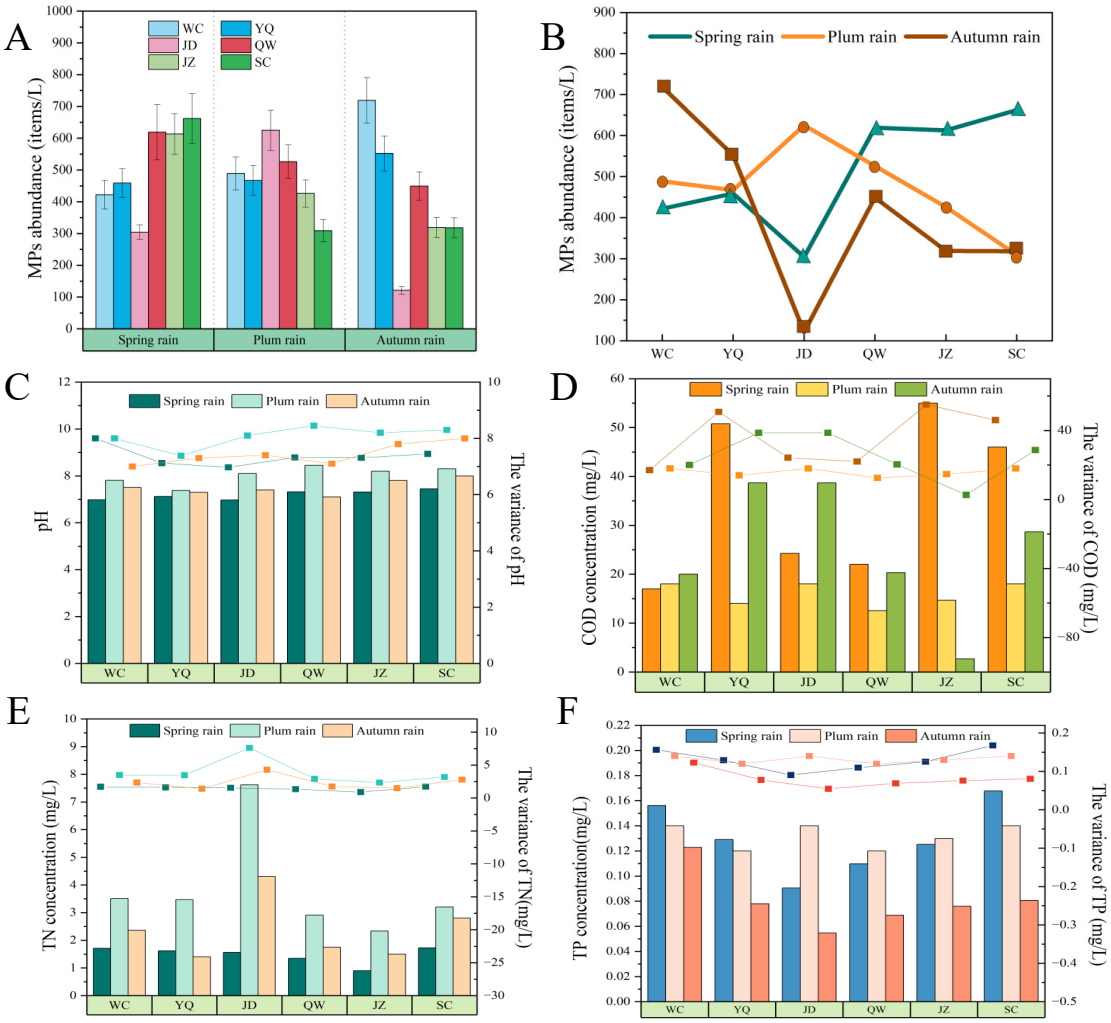


Figure 3. (**A**) Temporal distribution of microplastics in the rainy seasons. (**B**) Temporal variances of microplastics in the sampling sites, and water quality parameters (**C**) pH, (**D**) COD, (**E**) TN, (**F**) TP in the studied rainy seasons.

Water samples were taken to investigate water quality parameters in the Qinhuai River (Figure 3C–F). The pH concentration exhibited a consistent level of stability across the sampling sites, which was consistent with TP and TN concentrations in autumn rain. For TP and TN concentrations, plum rain showed a relatively higher abundance than other rain seasons, which revealed that rainfall would increase the TP and TN concentrations. This phenomenon can be primarily attributed to the propensity of phosphorus to become immobilized within the soil, coupled with its facile horizontal transportation through particle-laden runoff during periods of intense rainfall. In the dry season, a substantial quantity of phosphorus readily accumulates on the soil surface. As heavy rainfall occurs, the previously accumulated phosphorus is mobilized into the river, causing a marked upsurge in phosphorus concentration within the river water during the rainy season. The scouring effect of early rainy season runoff exacerbates the presence of phosphorus in

surface water while diminishing the influx of phosphorus in the autumn rainy seasons with decreasing rainfall. Meanwhile, TN concentrations were volatile and higher in plum rain than in other seasons, while the COD was more stable in plum rain seasons. Overall, different seasons perform different rainfall characteristics.

The variation in seasons at the six sampling sites is likely affected by a combination of factors, including the shape, composition, and concentration of microplastic particles. The interplay of these parameters, along with the speed of water flow and variations among seasons, influenced the distribution patterns of microplastics during distinct periods of rainfall. Therefore, an analysis was conducted on the components of different microplastics to see if their properties affect the seasonal distribution of microplastics, as shown in the subsequent findings.

3.3. The Characteristics of MPs

Analyzing the physical characteristics of microplastics is crucial since it offers valuable information on pollution in urban rivers. Moreover, these characteristics influence how microplastics engage with and stick to other contaminants, resulting in the release of plasticizers and the promotion of microbial proliferation [45]. Figure 4 depicts the characteristics of MPs in the QH River by dimensions and color.

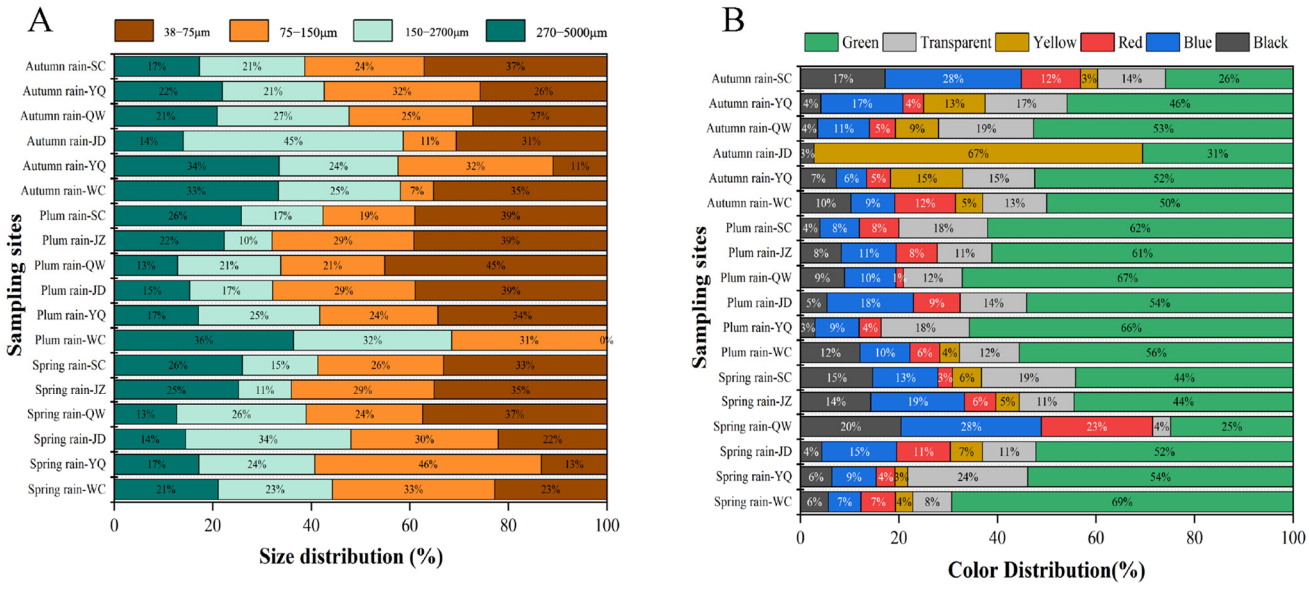


Figure 4. (**A**) Size and (**B**) color distribution during different rain seasons.

The size ranges of microplastics in the QH river are illustrated in Figure 4A, with sizes ranging from 270 to 5000 μm, 150 to 270 μm, 75 to 150 μm, and 38 to 75 μm. The characteristics of MPs in the surface water varied with the different seasons of rainfall. In the spring rain, the absolute predominance of MPs was small- and medium-sized. The prevailing sizes of microplastics (MPs) were predominantly tiny, ranging from 38 to 75 μm, constituting 13–37% upstream and 11–35% downstream, followed by a size of 75–150 μm with a percentage of 7–46% downstream. Organisms increase the bioavailability of small-sized MPs by consuming them [46], which poses an environmental risk to the downstream area of the QH River. In contrast, the large-sized MPs occurred more in plum rain seasons, while MPs with sizes of 150–270 μm and 270–5000 μm performed more in site WC upstream gradually. In autumn rain, the large-sized MPs of 270–5000 μm increased upstream and midstream, with a relatively balanced abundance in different sampling sites, which indicated that large microplastics were increasing while smaller microplastics may decrease in abundance with time.

The microplastics found in Qinhuai River exhibited a variety of colors, such as yellow, red, transparent, green, blue, and black (Figure 4B). Throughout all seasons, the predominant color was green, which occupied 25–69%. Blue and transparent microplastics exhibit greater prevalence compared to colored plastics, corroborating previous research findings [47,48]. Seasonal variation significantly influenced the color of microplastics. The dominant colors were blue, black, and yellow, which occupied 7–28% of blue and 4–20% of yellow in spring rain, and 3–67% of yellow in autumn rain. Previous studies also found that the occurrence of microplastic color was predominantly observed in green and transparent forms [49], suggesting a potential correlation with population behavior in specific regions. Transparent MPs were more even in many sampling sites and seasons, accounting for around 8–24% in spring rain seasons, 11–29% in plum rain, and 13–19% in autumn rain, respectively.

Figure 5A displays the visual appearance of microplastics, and the distribution of microplastics is depicted in Figure 5B. The most commonly observed forms of microplastics in the QH River are granules, followed by fragments. The results indicate a high occurrence of granules and fragments in urban rivers, highlighting the importance of recognizing the substantial impact of granular and fragment microplastics in urban rivers. Interestingly, granule dominates in spring rain and plum rain, accounting for 46~90%, while fragment predominance in autumn rain with a percentage of 81~96%. Seasons variation showed a significant impact on the shapes of microplastics. Previous research has also confirmed that granules and fragments are the prevailing components in both seawater and river sediment [50]. Granules primarily stem from the usage of cleaning and cosmetic products, along with the breakdown of larger biodegradable plastic materials [51]. Concurrently, there was a noticeable upward tendency in fiber change during the spring and plum rain seasons. The presence of microplastic fibers in home trash greatly contributes to the discharge of microplastic pollution, resulting in a significant impact. Furthermore, it is probable that fiber-like microplastics will arise from big plastic blocks, which are vulnerable to temperature changes, wind, water flow, and abrasion by hard objects during migration. Therefore, the spring and autumn seasons produce more garbage with heavier volumes of clothing, producing more fiber MPs, which aligns with the elevated concentration of larger-sized microplastics during the autumn rainy season.

ATR-FTIR spectra indicated the existence of several polymer types, and the polymers of MPs in the QH river are shown in Figure S1. Among the 60 selected microplastic samples per month, 51–55 were identified as microplastics, with a detection rate of 85–91.67%. In the results of the Qinhuai River, the variety of polymer types found in the microplastics over both seasons suggests the wide range of sources of microplastics. In the conducted research, the dominant polymers were polyethylene (PE), succeeded by polypropylene (PP), accounting for 13–40% and 22–50%, respectively (Figure 5C). The findings were strongly correlated with the performance, utilization, and cost of these polymers. Polyethylene (PE) is utilized in the production of personal care products like body and facial cleansers and the manufacturing of water bottles, food containers, and single-use plastic bags. Polyethylene terephthalate (PET) and polypropylene (PP) are commonly identified as microplastics in various river systems [52]. Notably, there is an increase in PET during autumn rain and spring rain but a decrease during plum rain. Polyethylene terephthalate (PET) is extensively utilized in the manufacturing of synthetic clothes and other textiles, serving as the main material for the production of plastic bottles [53]. Several factors influence the seasonal distribution of PET, including its peak density of 1.37 g cm^{-3}, as well as changes in precipitation and river runoff associated with climate change. In contrast, PVC is more prevalent in sampling sites with the seasons changing, accounting for thrice in spring rain and plum rain, and five times in autumn rain, respectively. The cost-effectiveness of PVC makes it a preferred material for agricultural film and fishing instruments in aquatic biological culture, particularly during the autumn rain seasons.

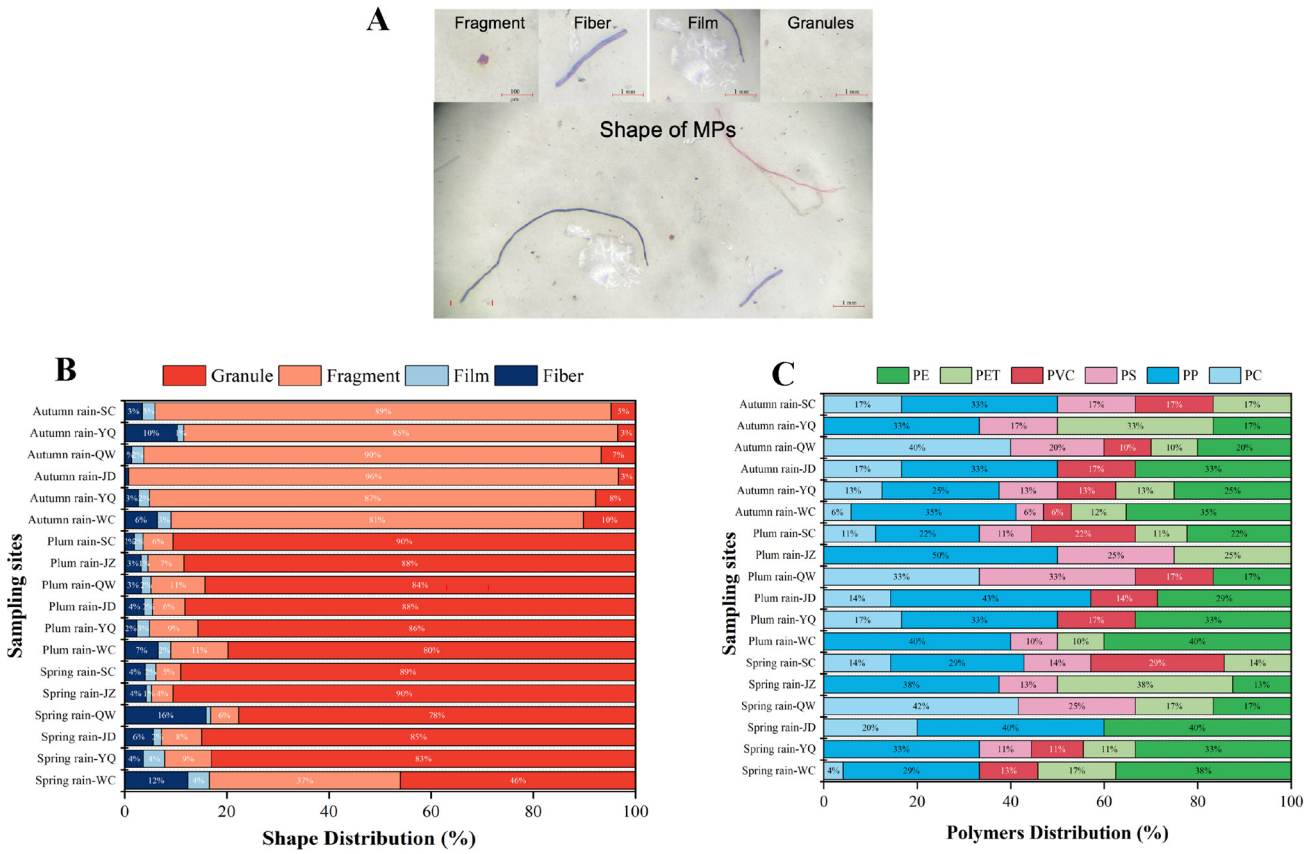


Figure 5. (**A**) Photographs of typical microplastics identified by microscopes. (**B**) Shape distribution during different rain seasons, and (**C**) compositions of the selected items in surface water of the Qinhuai River, China.

3.4. Risk Assessment of Microplastics

The toxicity of microplastic polymers varies based on their chemical composition, and polymers have varying toxic effects. The risk values for each sampling site were determined using formula (1), as indicated in Figure 6A and Table S4. Comparing the different sampling sites, most of the study areas had severe pollution levels (IV) in the studied seasons, and the overall pollution of the Qinhuai River is more severe. The toxicity ratings of certain polymers were found to be significantly higher than those of other polymers. This suggests that the toxicity of the polymers had an important impact on *H*-values and was a determining factor in the level of MP contamination in the research area. A few microplastics reached mild pollution (I), such as in the three rain seasons of site JZ and the plum rain season of site WC, while a few microplastics were at heavy pollution levels (III), such as the site WC in the autumn rain season and QW in spring rain season. Comparing the different rainfall periods, plum rain relatively reduced the risk of microplastics, with two sites exhibiting mild risk (I). In contrast, both spring and autumn rain had heavy pollution levels (III).

As can be seen from Table S3, PVC and PC are assessed to pose higher risks compared to PE, PS, and PA, whereas the risk index for PP and PET is considered negligible. PVC and PC are identified as the most detrimental microplastics to organisms; thus, the high level of MP contamination in the studied river area is severe. Excluding PC and PVC content, the seasonal effects are more pronounced in Figure S1 and Table S5, with mild pollution (I) in most detected rain seasons. For example, sampling sites of autumn rain were all at mild pollution (I), while few plum rain and spring rain season sites were categorized as slightly pollution (II). In summary, the Qinhuai River needs to be protected from the threats of PC and PVC, and the risk of plum rain has shown a decreasing trend in the three rainfall seasons.

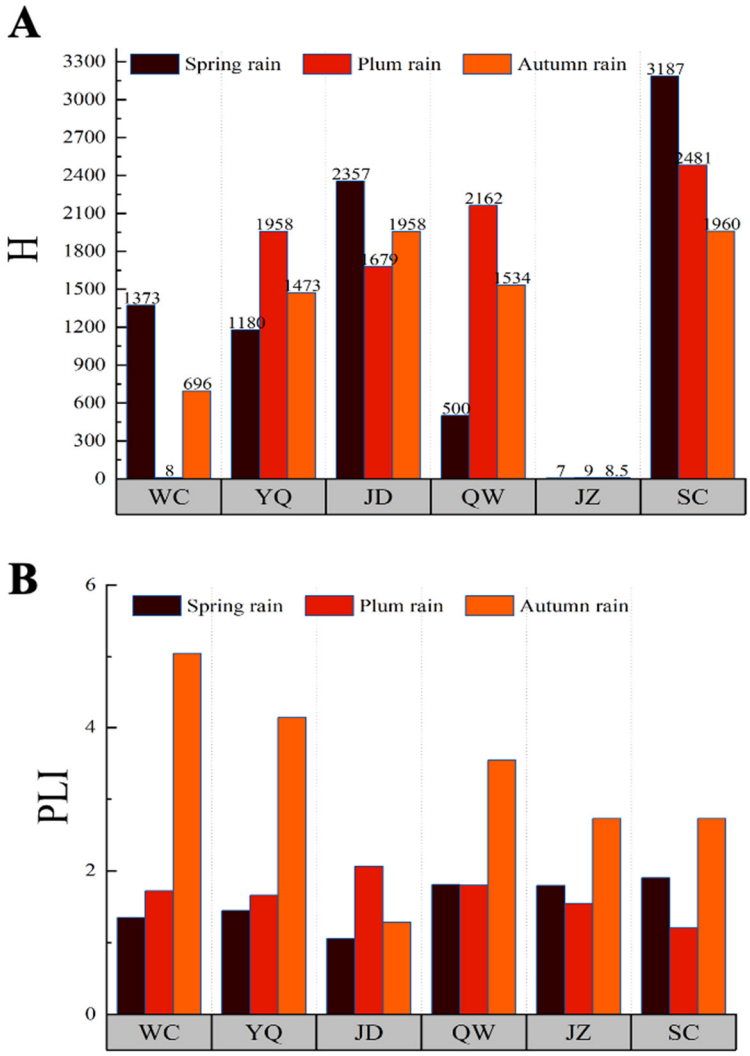


Figure 6. The potential risk index of various types of polymer microplastics in the Qinhuai River (**A**) hazard scores of plastic polymers (*H*), and (**B**) pollution load index (*PLI*).

The *PLI* value of each sampling site was determined using Formulas (2)–(4), and the results were displayed in Figure 6B. The sampling sites of three rain seasons were slightly polluted (I) in the Qinhuai River. The *PLI* was computed by utilizing the baseline microplastic concentration (C_{0i}), which is highly correlated with surrounding microplastic concentrations, flow rates, and human activities and determined by the minimum microplastic concentration. The particular values showed that the *PLI* value in autumn rains was relatively higher than in other seasons. The findings were also similar to the previous study in northern China, which revealed that PLI in the dry season were higher than wet season [54]. The primary reason for this trend is the lower average level of MPs in autumn rain seasons (Figure 3A), which increases the variation of the season fluctuations. The results were consistent with the previous study that the pollution load may change with seasonal changes [55]. Simultaneously, Table S6 displays a substantial correlation between the *PLI* result and the choice of the C_{0i} value, which was determined by using the average concentration as the C_{0i}. In order to fully understand the ecological risk assessment of the Qinhuai River, more research on risk evaluation is required to summarize polymer types, toxicity, or hazard scores of microplastics.

The study still has limitations in the current research. The toxicity of polymer monomers only partially correlates with their overall risk due to differences in the bioavailable fraction. At present, there are various risk assessment methods for microplastics and a lack of detection standards. Moreover, the selection of suspected microplastic particles

for component identification is often arbitrary, which can result in the potential underestimation of hazardous microplastics. Due to the increase in plastic consumption, managing microplastic pollution is a long-term challenge that requires international cooperation and collective effort.

4. Conclusions

This study investigated the distribution of microplastics (MPs) in the Qinhuai River in Nanjing City during an experimental period. It focused on examining the spatial distribution and seasonal characteristics of MPs during rainy seasons. The presence of MPs initially declined midstream and subsequently increased downstream, with a mean concentration of 466.62 ± 153.69 items/L. Microplastic abundance was vulnerable to fluctuation in different rainfall seasons; a higher MP concentration was found downstream of spring rain and upstream of autumn rain. Interestingly, the plum rain season inflicts a more stable variance of microplastics in different sites but with relatively higher concentrations of TP and TN. For the characteristics of MPs, fibers, PET, and large-sized (270–5000 μm) MPs occurred more in autumn rain seasons. Based on the abundance and polymer types of MPs, the risk index of *H* and *PLI* were at severe pollution levels (IV) and slightly polluted (I). The ecological risk of microplastics in the Qinhuai River should be seriously considered, and further studies are needed to examine the impact of microplastics on the ecological assessment in urban rivers. More monitoring approaches could be used to collect and detect MPs, such as the collection of filter screens and in situ pumps and the chromatography detection of Pyr-GC-MS and TED-GC-MS.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w16131857/s1, Figure S1: ATR-Fourier transform infrared spectra (FTIR) of the selected microplastics; Figure S2: The potential risk index of different polymer type (Delete PC and PVC); Table S1: Sampling locations for microplastics of Qinhuai River in Nanjing, eastern China. Table S2. Hazard scores for microplastic polymers. Table S3. Categories employed in the microplastics polymeric risk assessment (H), pol-lution loading index (PLI). Table S4. Risk level criteria for microplastic pollution. Table S5. Risk level criteria for microplastic pollution (Exclude PC and PVC content). Table S6. The value of the pollution load index in each sampling sites (C_0i takes mean value of 280 items/L, 237 items/L and 83 items/L in Spring rain, Plum rain and Autumn rain, respectively).

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