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Distribution and characteristics of microplastics in the basin of Chishui River in Renhuai, China

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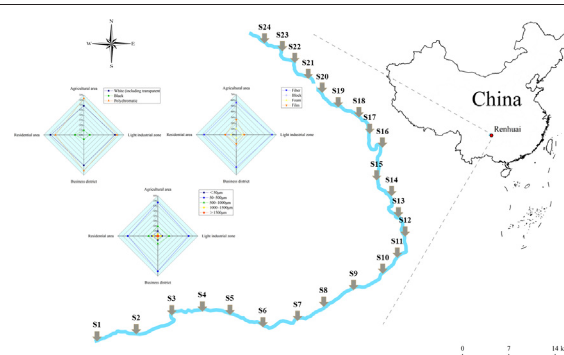
HIGHLIGHTS

- It is the first time to investigate the microplastics in Chishui River.
- Urban regional planning has an impact on the characteristics of microplastics.
- The local economic structure has a great impact on the microplastics.
- The risk index of the basin is 111.79, which belongs to the second risk area.

GRAPHICAL ABSTRACT



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ABSTRACT

As an emerging pollutant, microplastics widely exist in rivers all over the world. Due to the differences of economic development, economic structure and population in different regions, the abundance of microplastics in rivers is different. In those areas where agriculture is developed, the content of film microplastics is more, while in densely populated areas, the content of fibrous microplastics is more. Taking Renhuai Basin of Chishui River as the research object, the pollution characteristics and current situation of microplastics in the basin were analyzed, and the contamination risk of microplastics was evaluated. The abundance of microplastics in Renhuai basin of Chishui River ranges from 1.77 to 14.33 items/L. The main forms of microplastics were fibrous (59.4%), white (including transparent) (41.3%) and polychromatic (44.1%). The particle size of microplastics was mainly 500– 1000 μm (63.9%). According to the assessment, the risk of microplastics in the basin is 111.79, which is a secondary risk area. This study can provide a further reference for understanding the pollution characteristics of microplastics in rivers.

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1. Introduction

Plastic has a series of good properties and low price in our daily life (Hohn et al., 2020). However, due to the large-scale use of plastics (Zhang et al., 2020), many environmental problems have been caused (Malizia and Monmany-Garzia, 2019), and microplastic pollution is

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one of them (Ding et al., 2019). The size of microplastics is very small (<5 mm), so it has a large specific surface area (especially after aging and crushing) (Ding et al., 2020; Mao et al., 2020b), so it can adsorb heavy metals and other pollutants in the environment and enhance its toxicity (even some studies have shown that microplastics pollution can reduce the reproductive capacity of marine organisms) (Jaeseong and Jinhee, 2019), which has attracted more and more scholars' attention (Mao et al., 2020a).

In the study of river microplastics, the results reported at present mainly attach importance to the economically developed regions and the areas with more developed aquaculture. For example, in the investigation of Pearl River in Guangzhou, the abundance of microplastics is closely related to population density (Lin et al., 2018); in the survey of Yulin River in China, the abundance of microplastics is related to the width of waterway (Mao et al., 2020c); in the survey of Winnipeg Lake in Canada, the abundance of microplastics is closely related to the degree of industrial development (Anderson et al., 2017). These examples represent that there is a certain relationship between the abundance of microplastics and the level of regional economic development and man-made environment. It is this series of influencing factors that lead to great differences in the types and sources of microplastics in different regions.

The Chishui River, also known as Chishui, is a tributary of the upper reaches of the Yangtze River in China. This study is aimed at the investigation of microplastic pollution in the Renhuai Basin of Chishui River, China. The purpose of this study is: 1) to study the abundance, size, morphology and types of microplastic pollutants in Renhuai watershed of Chishui River; 2) to explore the correlation between the concentration of microplastics and urban functional zoning; 3) to assess the environmental risk of microplastic pollution in Renhuai watershed of Chishui River.

2. Materials and methods

2.1. Study area

Renhuai City, located in the northwest of Guizhou Province, is located in the middle reaches of Chishui River. It covers an area of 1788 km^2 and is the hometown of Maotai liquor in China. This survey is to set up 24 sampling points in Renhuai Basin of Chishui River (Fig. 1 and Table S1).

2.2. Sample collection

We rinsed the sampling tools and containers with deionized water before sampling, water samples with a depth of 10 cm were collected in stainless steel barrels, after taking water from a stainless steel barrel, 30 L of surface water were filtered through a 75 μm screen, and the filter materials on the filtered screen were washed into a glass bottle with ultrapure water, ultrapure water was made in our laboratory. Three parallel samples were taken from each sampling point. In order to prevent the water sample from being polluted and to reduce the error, the sampling tools were washed with ultra pure water before each sampling. Before laboratory analysis, in order to ensure the stability of the samples, the water samples were stored in the refrigerator at 4 °C.

2.3. Separation of microplastics

In order to avoid the influence of organic matter in the water sample on the subsequent analysis and determination, 30% H_2O_2 (Sinopharm Chemical Reagent Co. Ltd) was added into the glass bottle containing water sample, placed in a constant temperature oscillation box, and vibrated at the frequency of 100 r/min at 60 °C for 12 h. After vibration,

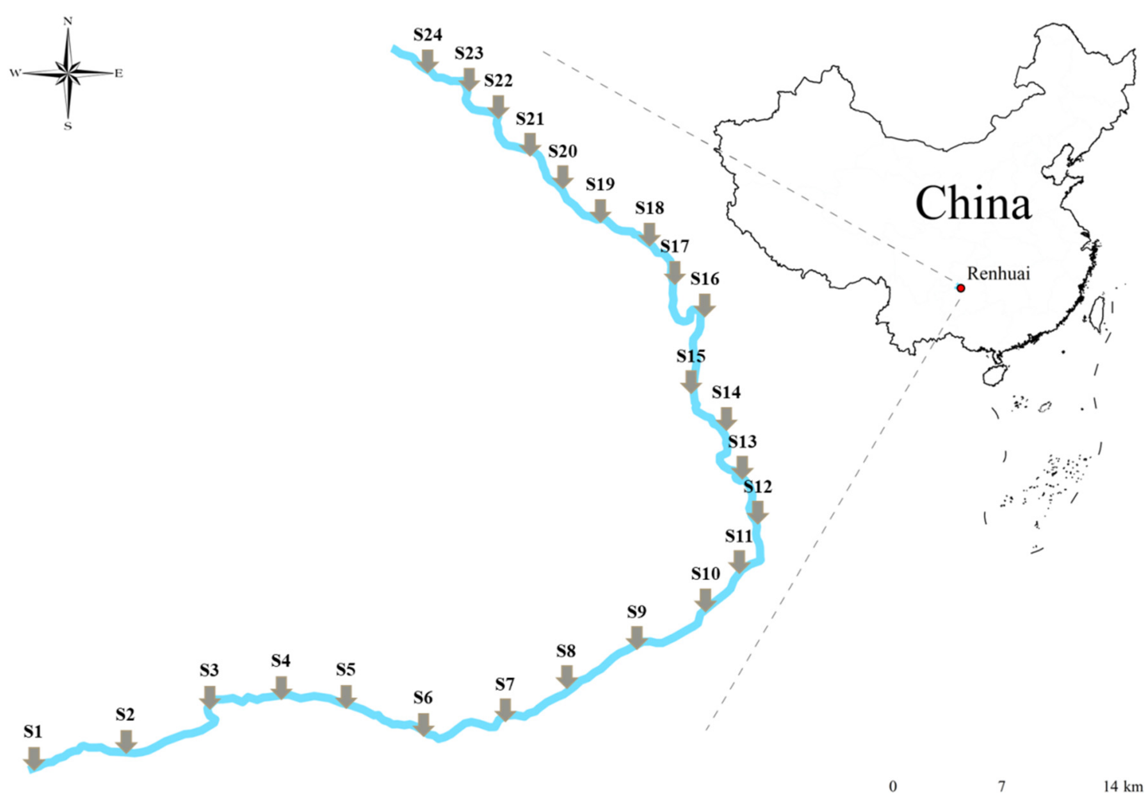

Fig. 1. Sampling point (S1-S24).

the supernatant was taken and filtered by vacuum pump through 0.45 μm filter paper. After filtration, all possible microplastics filter materials were retained on the filter paper. Put the filter paper into the culture dish cleaned with ultra pure water, and then put the culture dish in the oven to dry at 50 °C for 24 h. In the process of separation and identification of microplastics, in order to avoid the contact between samples and other plastic products, resulting in experimental errors, we used ultrapure water to clean all experimental equipment. In order to avoid the influence of dust and fine fibers in the air on the experimental results, we covered the samples with tin foil.

2.4. Observation and identification of microplastics

After the filter paper containing the filter material is dried, all suspicious microplastics on the filter paper were observed by metallographic microscope (MV500), the size and shape of the microplastic were identified and photographed according to the identification method in the previous research (Jesus et al., 2018). Recording the size of the microplastic (< 5mm) and shape (fiber, bulk, foam, film). The microplastics observed on the filter paper under microscope showed the following characteristics: 1) no fixed shape; 2) no obvious spatial structure; 3) uniform diameter (fiber). Some microplastics larger than 2 mm were selected from each sample, and a total of 150 suspected microplastics were selected for FTIR analysis. All microplastics smaller than 5 mm are recorded in the microscope. According to the different sizes, the microplastics were divided into six categories, i.e., <50, 50–500, 500–1000, 1000–1500 and >1500 μm, The microplastic larger than 2 mm were selected to verify their chemical structure by using a Fourier transform infrared (FTIR) spectrometer (Vetex70, Bruker) in attenuated total reflection (ATR) mode. The spectra were investigated and subtracted from the baseline in the scan range of 400–4000 cm^{-1} at a resolution of 2 cm^{-1}, and the obtained spectra were then compared with known polymer spectra to identify the polymer type.

In this study, the abundance of microplastics was measured by the amount of microplastics per liter, Microsoft Office Excel 2010 was used to analyze and calculate the data of each point, and origin-2018 was used for data chart drawing.

2.5. Quality assurance and quality control

In order to ensure the accuracy of the experiment, the nitrile gloves and cotton clothes were worn during the whole experiment and the analysis and determination process. All the utensils in the experiment were washed with ultra pure water. In order to determine the influence of reagents used in the experiment and the air environment in the laboratory on the results, we conducted a blank experiment. Vacuum filtration was carried out on 0.45 μm blank filter paper. The air in the laboratory was filtered for 60 min. The average number of microplastics observed on each filter paper was 0.23 ± 0.11. In addition, no plastic particles can be detected on 0.45 μm filter paper after vacuum filtration of 5 L ultra pure water. Because the number of microplastic particles detected in the blank experiment was very small, the influence of laboratory environment on the experimental results can be ignored.

2.6. Hazard index

As a new pollutant, the research on the harm of microplastics mainly focuses on the impact of microplastics on organisms. However, the risk assessment of microplastics in a specific area is still rare. Based on this gap, the risk index (H) of microplastics was used to evaluate the risk of microplastics pollution in surface water of Renhuai City. The specific formula is as follows (Lithner et al., 2011a):

$$H = \sum P_n \times S_n \tag{1}$$

where H is the risk index of the polymer; P_n is the ratio of the polymer concentration of various types of microplastics to the total concentration of the microplastics; and S_n is the hazard score of the plastic polymer. S_n of polypropylene (PP), polyethylene (PE), polystyrene (PS) and polyvinyl chloride (PVC) were 1, 11, 30 and 5001, respectively (Lithner et al., 2011b).

3. Results and discussion

3.1. Abundance and characteristics of microplastics

3.1.1. Abundance and distribution of microplastics

A total of 24 sampling points (S1-S24) were set up in Renhuai basin of Chishui River (Fig. 1 and Table S1). Laboratory analysis showed that microplastics were detected in each sampling point, indicating that the Renhuai basin of Chishui River had been polluted by microplastics. The abundance of microplastics ranged from 1.77 to 14.33 items/L (Fig. 2 and Table 1). There are some differences in the abundance of microplastics in each sampling point. As can be seen from Fig. 2, the microplastic graduation of the 24 sampling points from S1 to S24 shows a downward trend. S4 and S5 are located in the agricultural area, and the agriculture in Renhuai City is relatively developed. The high abundance of microplastics in these two sampling points may be due to the large amount of agricultural plastic films used (Tien et al., 2020; Wurm et al., 2020). The S7 and S8 sampling sites are located in the light industrial zone. As the capital of liquor in China, Renhuai City has a complete liquor industry chain. The high abundance of microplastics in these two sampling points may be caused by the outer packaging used after liquor production (Gaoliang et al., 2021).

By comparison with other inland rivers, the abundance of microplastics in the Renhuai basin of Chishui River is in the middle and upper level. Compared with the Three Gorges reservoir (Di and Wang, 2018), the abundance of microplastics in Renhuai basin of Chishui River is slightly lower than that of Amsterdam canal (Leslie et al., 2017), much lower than that of Galleting River in the United States (Barrows et al., 2018), and much higher in Renhuai basin of Chishui River compared with Antua River (Rodrigues et al., 2018), Tibet Plateau River and Hangjiang river (Changbo et al., 2019). Interestingly, as the upper reaches of the Yangtze River, the abundance of microplastics in Renhuai basin of Chishui River is slightly higher than that in the Yangtze River Estuary (Shiye et al., 2014). This may be caused by a series of factors. Some studies have shown that the uneven distribution of microplastics in rivers is closely related to human factors and hydraulic characteristics (He et al., 2020). The faster the river

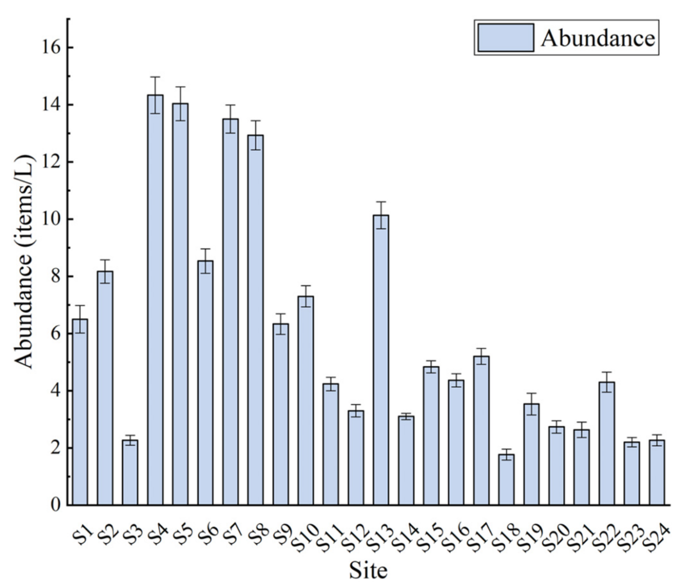

Fig. 2. Abundance of each point (S1-S24).

Table 1
The abundance of microplastics at each sampling point.

Site	Abundance (items/L)	Error (items/L)
S1	6.50	0.48
S2	8.17	0.41
S3	2.27	0.17
S4	14.33	0.64
S5	14.03	0.59
S6	8.53	0.43
S7	13.50	0.49
S8	12.93	0.51
S9	6.33	0.36
S10	7.30	0.37
S11	4.23	0.24
S12	3.30	0.22
S13	10.13	0.47
S14	3.10	0.11
S15	4.83	0.21
S16	4.37	0.23
S17	5.20	0.28
S18	1.77	0.19
S19	3.53	0.38
S20	2.73	0.22
S21	2.63	0.27
S22	4.30	0.35
S23	2.20	0.16
S24	2.27	0.19

velocity is and the longer of microplastic soaking in the river, the lower the abundance of microplastics (Zhou et al., 2020).

3.1.2. Morphological characteristics of microplastics

In the course of the microscopic observation stage, the microplastic colors observed were white, transparent, black, blue, green, and red. As the number of microplastics in blue, green, red and transparent colors was insignificant, the final classification was divided into three types: White (including transparent), black and polychromatic. The abundance of microplastics with different colors at each sampling point is shown in Table S2 of the Supplementary information. The color diversity of microplastics also indicates the diversity of pollution sources (Dongdong et al., 2020). Among them, white (including transparent), polychromatic and black microplastics accounted for 41.3%, 44.1% and 14.6% respectively (Fig. 3a). White (including transparent) and multicolor microplastics occupy the majority in the whole, and polychromatic microplastics are slightly more than white (including transparent), while black microplastics occupy relatively little proportion (Wenfeng et al., 2017; Zhang et al., 2015).

There are two main sources of white microplastics. On the one hand, white plastic products such as plastic bags, nylon nets and the use of plastic film in cultivated land will produce a large number of white microplastics. On the other hand, polychromatic microplastics are weathered and discolored by light, heat, water and biological action in water, thus forming white microplastics, which may be an important source of white microplastics (Galafassi et al., 2019; Kecheng et al., 2019; Liu et al., 2020). In addition, polychromatic microplastics were found in all sampling points, and there were quite a few kinds of colors, which indicated that the pollution sources of these microplastics were overwhelmingly wide (Xiaoyun et al., 2018).

In this study, according to previous literature research (Shiye et al., 2014), the shape of microplastic can be divided into four types: fiber, bulk, foam and film (Fig. 4 and Table S3). The ratio of microplastic to fiber, block, foam and film is 59.4%, 11.7%, 11% and 17.9% respectively (Fig. 3b).

It can be seen from the proportion of types, as a typical microplastics, the proportion of fibrous microplastics is the largest, which is consistent with the previous research results of microplastics (Ahmet et al., 2021). Studies have shown that a liter of laundry wastewater may contain more than 100 kinds of plastic fibers, which municipal sewage pipes transport to rivers (Anthony et al., 2011). There are human activities along the Renhuai Basin of Chishui River, and there is a national road along the river. These fibrous microplastics may come from the waste water from washing human clothes (Edgar et al., 2017), wear products of automobile tires (R and E, 2019) and suspended atmosphere (Xuemin et al., 2019). Compared with other rivers in the study, the fibrous microplastics in Renhuai basin of Chishui River did not originate from fishing activities (Di and Wang, 2018), because the whole Renhuai basin of Chishui River was closed to fishing. The block microplastics may have come from frosted particles in bags and plastic containers, as well as in cleaning products that people use (Antunes et al., 2013; Hidayaturrahman and Lee, 2019). Foamed microplastics are relatively small in size and irregular in shape. Because of their excellent impact resistance and thermal insulation properties, foams are widely used in thermal insulation, construction, packaging and manufacturing industries (Egessa et al., 2020; Wen et al., 2018). Therefore, these foams may be produced by packing cushions and insulation materials of various products. Films microplastics may come from plastic products used in agricultural planting, such as agricultural film and impermeable plastic film, or they may be broken from improper treatment or discarded plastic bags (Gaoliang et al., 2020).

We classified the observed microplastics into five types according to their sizes: <50, 50–500, 500–1000, 1000–1500 and >1500 μm. The proportions of these five types of microplastics were 9.3%, 63.9%, 20.9%, 4.8% and 1.1%, respectively (Fig. 3c), it can be seen from these data that the proportion of microplastics with the size of 50–500 μm is the most, and that of microplastics larger than 1500 μm is the least (Table S4). This is because the larger size of microplastics can produce a number of smaller size fragments during degradation, so the larger abundance is often the small and medium-sized microplastics (A et al., 2014). In addition, due to the limitation of experimental instruments, the microplastics with smaller particle size may not be fully detected.

3.2. Analysis of urban functional zoning

The Renhuai basin of Chishui River is divided into four urban functional zones, namely agricultural area (S1–S6), light industrial zone (S7–S16), business district (S17, S18) and residential area (S19–S24). The average abundance of microplastics was 8.97, 6.69, 3.48 and 2.83

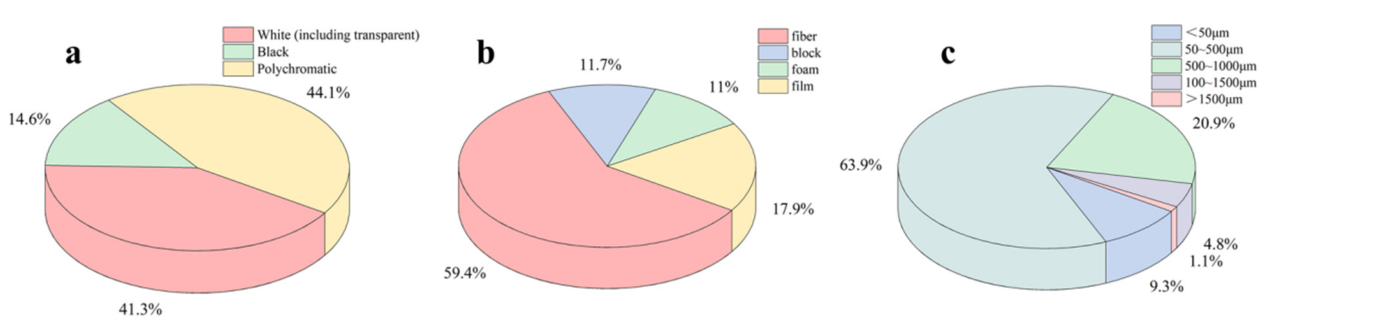

Fig. 3. Proportion of color (a), shape (b) and size (c) of microplastics.

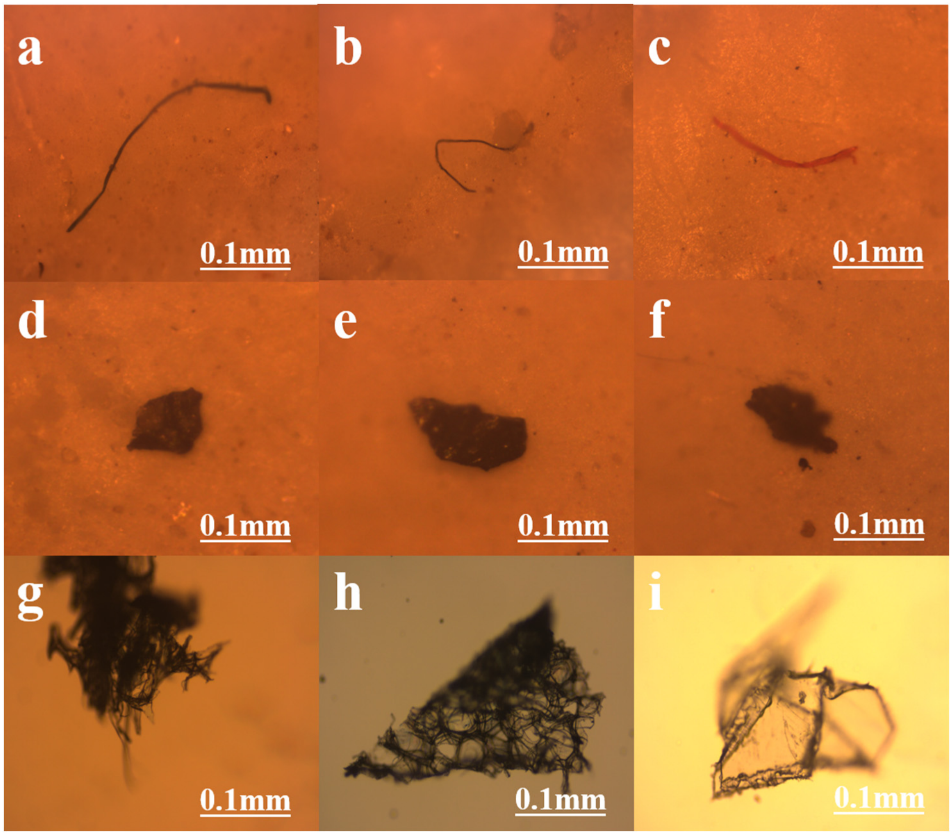

Fig. 4. Typical microplastics, fibers (a, b, c), lumps (d, e, f), foams (g, h), and films (i) observed in metallographic microscope.

items/L, respectively (Fig. 5). This may be because there is no heavy industry in Renhuai basin of Chishui River, and the population is not large, and agriculture is relatively developed, so the abundance of microplastics detected in agricultural area is the highest (Prata, 2018).

The proportion of microplastic shape classification detected in each functional area is shown in Fig. 6. From Fig. S1 in the Supplementary information for the proportion of microplastics with different shapes at each sampling point, it can be seen that, whether in agricultural areas, light industrial areas, commercial areas, residential areas, fibrous microplastics account for the largest proportion, which is also consistent with the previous research (Su et al., 2016; Wang et al., 2017; Zbyszewski et al., 2014). Moreover, the proportion of fibrous microplastics in each functional area is not obvious, only the proportion of fibrous microplastics in light industry area is slightly higher, which may be caused by the production of light industry. In addition, the proportion of plastic film in the agricultural area is higher than that in other functional zoning. This may be due to the

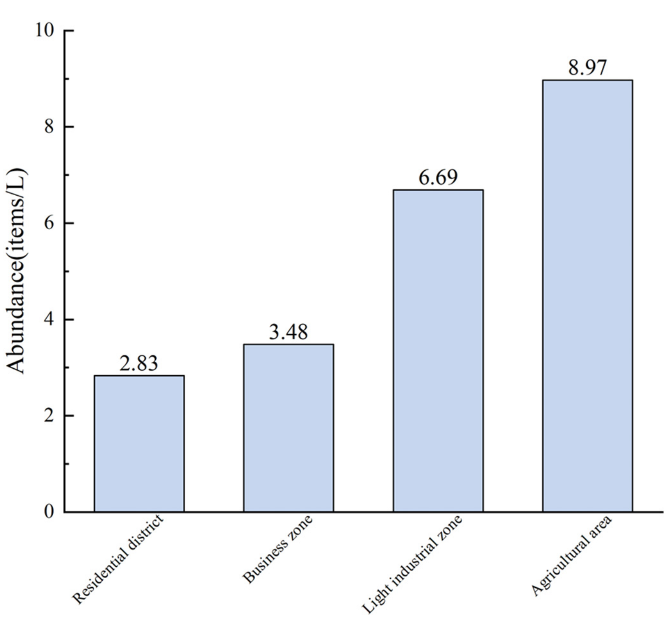

Fig. 5. The abundance of microplastics in each functional area.

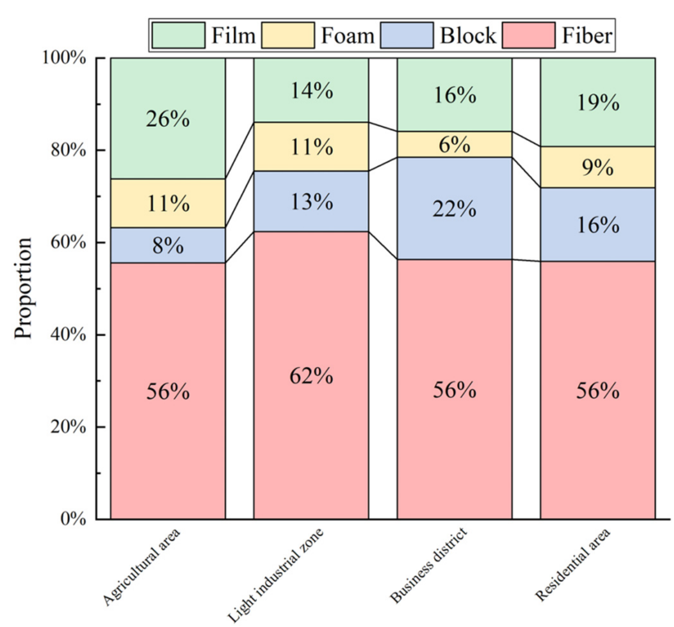

Fig. 6. Proportion of microplastics shape classification in each functional area.

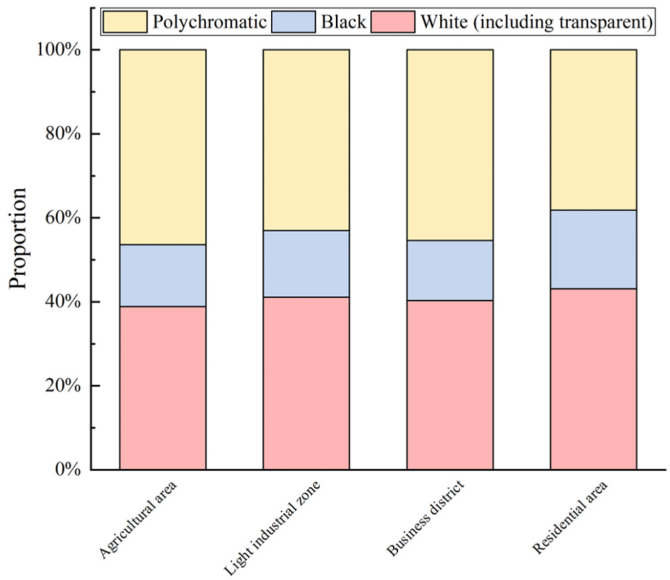

Fig. 7. Proportion of microplastics color classification in each functional area.

large area of agricultural film used in the production of rice and other agricultural products (Wurm et al., 2020).

The proportion of microplastic color classification detected in each functional area is shown in Fig. 7. From Fig. S2 in the Supplementary information for the proportion of microplastics with different colors at each sampling point, it can be seen from the data and figures that the proportion of white (including transparent) and polychromatic microplastics is not different in all functional areas, and the proportion of polychromatic microplastics is slightly higher than that of white (including transparent) microplastics, while the proportion of black microplastics is relatively small. White (including transparent) microplastics come from a wide range of sources, while multicolor microplastics may come from colorful plastic packaging and cosmetics used in people's production and life (Abbasi and Turner, 2021). In addition, Renhuai, located in Zunyi City, Guizhou Province, is a famous liquor producing area in China. Therefore, more multicolor microplastics may be produced in the production and packaging stage of liquor products. There is no significant difference in the proportion of microplastics in the same size range among different zones. The proportion of microplastics with the size of 500–1000 μm is the highest, and that of more than 1500 μm was the least (Fig. S3).

3.3. Polymer types and risk assessment of microplastics

Similar to many other inland river studies (Anh et al., 2020; Aparna et al., 2020; Chao et al., 2021), the main types of microplastics detected in the Renhuai Basin of Chishui River are PE (36%), PP (31%), PS (25%), and a small amount of PVC (2%) (Fig. 8). Due to the limitation of experimental instruments (FTIR), we may not have detected all types of polymers, which may lead to some errors in the experiment.

Four kinds of microplastics, such as PE, PP, PS and PVC, have been detected in Renhuai Basin of Chishui River, which fully indicates that the production and living of human beings along the river basin have caused plastic pollution to the river. These four polymers are characterized by low prices, tremendous output and wide application range (Köfteci et al., 2014), so they are widely used in production and life.

According to the risk assessment method mentioned above, the risk index (H) of Renhuai Basin of Chishui River is 111.79. According to the previous research, the risk level of microplastics is divided into four categories: I, II, III and IV. The higher the level is, the greater the risk of microplastic pollution (Li et al., 2020). The risk category of microplastics in Renhuai City is class III, which is higher than that in Jianyang, Luzhou,

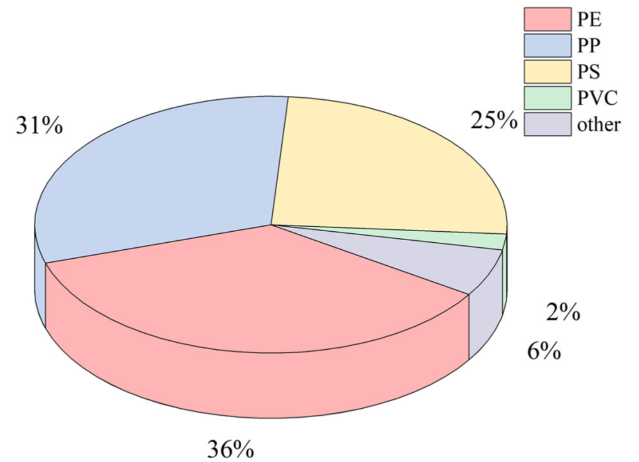

Fig. 8. Polymer types of microplastics.

Jintang, Zizhong and Neijiang in China, and in the same risk category as Ziyang and Fushun in China (Zhou et al., 2020). Therefore, the impact of microplastics should be took into account in the future ecological risk assessment of pollutants in Chishui basin.

4. Conclusions

Renhuai Basin of Chishui River is polluted by microplastics. The pollution characteristics and current situation of microplastics were analyzed. This study fills the gap of Chishui River microplastic pollution, and evaluates the risk of microplastic pollution in Renhuai City. However, the occurrence of microplastic pollution in different seasons and climate conditions needs further study. In addition, as a new type of pollutants, there is not a uniform evaluation standard to evaluate its harmfulness and environmental risks. It is hoped that more models can be used in real life to evaluate this worldwide problem.

CRediT authorship contribution statement

Jianlong Li: Writing - original draft. **Zhuozhi Ouyang**: Writing - review & editing. **Peng Liu**: Data analysis. **Xiaonan Zhao**: Data analysis. **Renren Wu**: Sampling and Review. **Chutian Zhang**: Editing. **Chong Lin**: Editing. **Yiyong Li**: Editing. **Xuetao Guo**: Conceptualization, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.145591.

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