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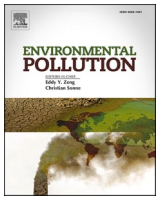

Interactive effect of urbanization and flood in modulating microplastic pollution in rivers☆

Aline Reis de Carvalho [a,b,*], Louna Riem-Galliano [a], Alexandra ter Halle [b], Julien Cucherousset [a]

[a] UMR 5174 EDB (Laboratoire Évolution and Diversité Biologique), CNRS, Université Toulouse III Paul Sabatier, IRD, 118 Route de Narbonne, 31062, Toulouse, France
[b] UMR 5623 IMRCP (Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique), CNRS, Université Toulouse III Paul Sabatier, 118 Route de Narbonne, 31062, Toulouse, France

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ABSTRACT

Freshwater ecosystems play an important role in transporting and accumulating microplastics. Spatial and temporal variability in microplastic pollution can create critical spots and moments of elevated pollution, however, the consequences of their interaction are still poorly understood. This study aimed to assess the interaction between urbanization and flood episodes on river microplastic pollution. The water surface was sampled in two sites of the Garonne River, upstream and downstream a large urban area, during two flood episodes. Samples were chemically digested to facilitate particles isolation, and microplastics (700 μm–5 mm) were characterized through infrared spectroscopy (ATR-FTIR). Microplastic concentration increased by 5–8 fold during flood episodes, driven by river discharge. This increase was more significant in the downstream site. During the flood, there was an overall increase of larger particles on water surface, but only in the downstream site microplastic colours and polymeric compositions significantly varied. Principal component analysis of infrared spectra from polyethylene microplastics revealed that the main variance in the spectral region corresponded to hydroxyl and carbonyl groups. The carbonyl content in microplastics was significantly higher for particles collected during the flood, likely indicating a higher level of degradation. Urbanization modulates freshwater microplastic pollution during floods, and changes in microplastic physicochemical profile should be further integrated within toxicity studies to evaluate risks potentially elevated to animal and human health.

1. Introduction

Rivers play an essential role in the transport and temporal dynamics of global microplastic pollution (He et al., 2020; Reisser et al., 2015; Roebroek et al., 2021). In general, the concentration of microplastic particles, i.e., particles smaller than 5 mm (Andrady, 2011), in a river is expected to increase from upstream to downstream, with additional inputs from tributaries or inland activities accumulating in the main stream (Napper et al., 2021; Treilles et al., 2021). Land use is an important driver of the spatial distribution of microplastic in a catchment. For instance, urbanized areas have been consistently identified as important sources of microplastic to rivers, resulting in 'hotspots' of microplastic pollution (Chen et al., 2020; de Carvalho et al., 2021a; Dris et al., 2015; Grbić et al., 2020). Furthermore, temporal variations in freshwater microplastic pollution might also occur, mainly modulated by hydrological conditions. High discharge events can affect microplastic pollution by inducing abrupt remobilization of settled particles accumulated in the riverbed (Hurley et al., 2018). This could be associated with an increased microplastic concentration in the water column, reinforced by additional inputs from the floodplain (Christensen et al., 2020). Therefore, the temporal dynamics of microplastics is characterized by the occurrence of "hot moments" of pollution (Hitchcock, 2020; McClain et al., 2003; Treilles et al., 2021). The increase in microplastic concentration due to increased river discharge can be regulated by land-use (Wagner et al., 2019), but further investigations are needed to better understand this interactive effect on microplastic pollution profile in streams.

Microplastics are considered a complex contaminant because they are characterized by a myriad of combinations of physical (i.e. size, morphology, colour) and chemical (i.e. polymer, oxidation level, chemicals associated content) properties (Rochman et al., 2019). Floods not only change microplastic concentration, but also affect the

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* Corresponding author. Current address: UMR 6282 Biogéosciences, CNRS, université Bourgogne Franche-Comté, 6 boulevard Gabriel, 21000 Dijon, France.
E-mail address: aline.de-carvalho@u-bourgogne.fr (A.R. de Carvalho).

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physicochemical profile of this pollution. Temporal changes in the diversity of microplastic composition might be influenced by the predominance of a specific source. For instance, the proximity with a highway would increase the proportion of tire wear particles in streams following a flood (Horton and Dixon, 2018). Also, greater diversity in the composition of microplastics following floods is likely caused by a more diverse source of this contaminant (Gündoğdu et al., 2018). Once in the stream, the hydrodynamics of microplastics is regulated by their physical and chemical properties such as particle size, density, and shape (Kowalski et al., 2016; Liu et al., 2020). Increased river discharge is associated with increased water energy, which can lead to a prevalence of larger and heavier particles at the water surface (Cheung et al., 2019). However, microplastic properties are often correlated (de Carvalho et al., 2021a) and accounting for the diversity of microplastic features is necessary to further investigate the dynamic of microplastic profiles in the environment (Rochman et al., 2019; Waldman and Rillig, 2020).

Weathering of microplastics in the environment causes changes in their physical and chemical properties (Barnes et al., 2009; Christensen et al., 2020; Gewert et al., 2015). For instance, higher oxidation states, commonly measured through the presence of carbonyl and hydroxyl contents, are observed in microplastics collected in the environment compared to virgin ones (Canopoli et al., 2020; Dong et al., 2020; Gewert et al., 2015). Several factors influence this photo-induced oxidative process, such as the type of polymer, the presence of additives, the residence time in the environment, and exposure to natural conditions, such as solar radiation (Delorme et al., 2021). Higher exposure to ultraviolet radiation and a consequent increase in photo-initiated oxidation reactions can result in more oxidized microplastics on land than those in water (Bond et al., 2018; Christensen et al., 2020; Xiong et al., 2017), where a slower oxidative process is observed (Karlsson et al., 2018; Liu, 2020; Tang et al., 2019). Microplastics might be perceived as carriers of environmental contaminants, such as pharmaceuticals and persistent organic pollutants (POPs), and pathogens in a process influenced by their weathering condition. Increased embrittlement, surface cracks, biofilm, and oxidation state are commonly associated with a higher concentration of these chemicals within a microplastic (Hossain et al., 2019; Kirstein, 2016; Naik, 2019; Wagner et al., 2014). The quantification of alterations in the chemical profiles of microplastics could therefore help to identify potential accentuated risks to the health of aquatic organisms.

The general aim of this study was to understand the interactive effect between flood and urbanization on the dynamics of microplastic pollution in streams. This was achieved by quantifying microplastic pollution during flood episodes upstream and downstream a large urban area (Toulouse, France). The first objective was to quantify changes in microplastic concentration. Our hypothesis was that microplastic concentration generally increases during flood episodes and that the urban area acts as a microplastics hotspot, sharpening this increase. The second objective was to quantify the changes in the profile of microplastic pollution during a flood. We hypothesized that urbanization affects microplastic pollution profile with a greater diversity of sources and, consequently, a greater diversity of microplastic composition and colours. We also hypothesized that larger particles would prevail on water surface during a flood, independently of urbanization, due to increased water energy and discharge. Finally, the third objective was to investigate changes in the infrared spectra of microplastics to reveal the impact of flood episodes and urbanization on the chemical profile of this pollutant.

2. Methods

2.1. Study area and sampling design

The Garonne catchment covers an area of 53.236 km^2 and is the third biggest catchment in France by its average flow. The main river has its source in the Pyrenees (Val d'Aran, Spain) and flows northwards through three main urban areas, Toulouse, Agen, and Bordeaux where it reaches the Atlantic Ocean. The climate over the south-eastern part of the Garonne basin is under the influence of a Mediterranean climate, characterized by high temperatures in summer. River discharge is strongly dependent on snowmelt and is also influenced by precipitations, typically resulting in heavy rainfall events in autumn and spring. Flood peaks mainly occurs in May–June, and a period of low flow is expected from summer to early autumn (Caballero et al., 2007; Lambs et al., 2009). In this study, two sites located in the mainstream were selected, upstream (Muret village, MUG, 43.45862 N and 1.327305 E) and downstream (Gagnac village, GSG, 43.70675 N and 1.361795 E) Toulouse (Fig. 1). To understand the potential role of tributaries in modulating microplastic pollution dynamics in the main stream, the most urbanized tributary with highest microplastic concentration (Hers river (de Carvalho et al., 2021a)), was also sampled (Launaget, LAU, 43.66534 N and 1.447144 E).

To understand the dynamics of floating particles during an increased discharge, a first sampling was performed on October 15th, 16th, 18th and 22nd, 2018 in the sites MUG and GSG (flood A, sampling events A1 to A4) (SI Fig. 1). A discharge peak of 336 m^3s^{-1} occurred in MUG on October 15th (SI Fig. 1a).

The interval between sampling events was adapted and a second sampling period was performed on April 24th, May 6th, May 22nd, June 05th, June 18th and July 3rd, 2019 in the sites MUG, GSG and LAU (flood B, sampling events B1 to B6) (Fig. 2). A discharge peak of 1190 m^3s^{-1} occurred in GSG on May 26th (Fig. 2b). Discharge fluctuations on Hers river during sampling period B prevented the establishment of a single flood episode in this stream (Fig. 2c). The sampling period B was considered for the investigation of microplastic profile.

2.2. Sample collection

Surface water samples were collected by filtration using a Manta trawl (opening 32 cm × 82 cm) equipped with a 500 μm mesh polyamide net and a removable cod-end with the same mesh size (de Carvalho et al., 2021a; Faure et al., 2015; Galgani et al., 2013). The 500 μm mesh was selected to maximize a trade-off between the volume of filtered water, net clogging, and particle size and concentration. During each sampling event, the Manta trawl was attached to a bridge guardrail over the river and immersed in the fast-flowing and deepest part of the river. The first 30 cm of water were sampled, except when the trawl was not fully submerged (shallow waters). In these cases, water level was measured and used to correct the volume of filtered water. Sample duration was approximately 10 min and was precisely recorded for each sampling. A propeller flowmeter (Hydro-Bios, Germany) was placed at the centre of net entrance for estimating the water flow that passed through the net. At each site, sampling was performed in successive triplicates. After each sampling, the cod-end content was sieved into a 500 μm mesh using river water and transferred to sealable plastic bags made of polyethylene, as performed by previous studies (Cheung et al., 2019; Wong et al., 2020). Considering the size range of particles in this study, contamination at this step was very unlikely. The diagonal of our 500 μm mesh net, i.e. 700 μm, was considered as the lower limit of detection for microplastics, once particles smaller than 700 μm could still pass through the pore size, affecting the robustness of the measurement. Samples were stored in a cooler in the field and stocked at 4 °C in the laboratory before subsequent analyses.

2.3. Sample treatment

At the laboratory, a protocol consisting of double-step organic matter digestion was applied to eliminate the organic matter content and facilitate microplastic recovery (see further details in de Carvalho et al., 2021c). Once several wash-and-filter steps were needed, an open cap equipped with a polyamide mesh of 500 μm, the same composition as

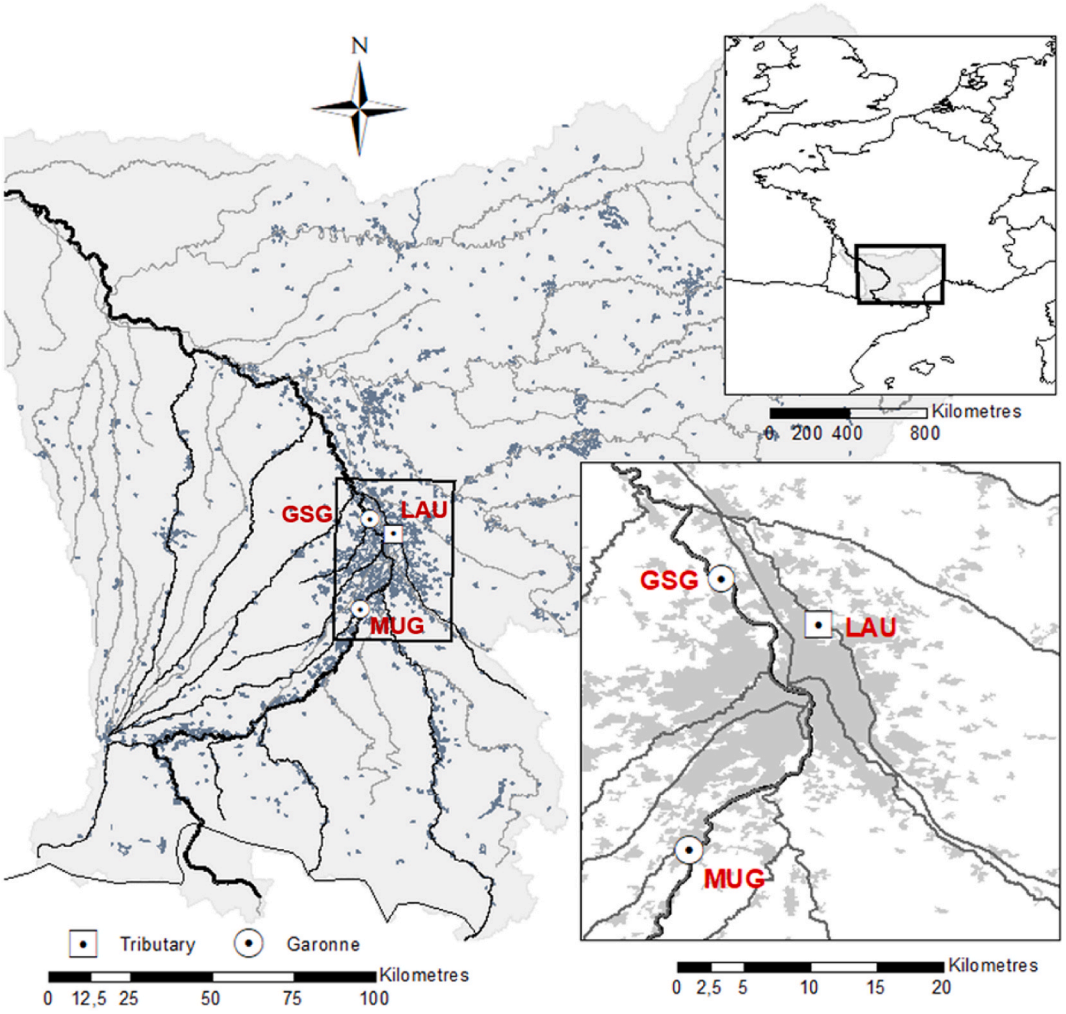

Fig. 1. Distribution of sampling sites in the study area.

the sampling device, was manufactured. Briefly, samples were incubated in a potassium hydroxide solution (KOH 10% (w/w)) in a proportion of 4 units of volume (mL) to 1 unit of sample (g), at 60 °C for 8 h. The digested content was filtered through the mesh and the remaining content was washed three times with pre-filtered distilled water to remove any residues of potassium hydroxide solution. Samples were incubated with hydrogen peroxide solution (H_2O_2 30% (w/w)) for 16 h at room temperature (de Carvalho et al., 2021c). The digestion procedure was able to eliminate, on average, 60% of the organic matter content (de Carvalho et al., 2021c). Then, samples were filtered and washed three times with pre-filtered distilled water and the mesh content was analyzed under a stereomicroscope (14-fold magnification, Leica MZ75 and Nikon SMZ800). Each sample was analyzed by two different operators, representing a good compromise between the time of analyses and particle recovery, totalizing an average inspection time of approximately 30 min per sample (de Carvalho et al., 2021c). Particles were recovered using metallic tweezers and temporally placed in a new and identified petri-dish over a paper filter. Fibre particles, mainly textiles, were not included as microplastic particles considered in this study due to the considerable amount of remaining organic matter which hampered the recovery of this type of particles.

2.4. Microplastic characterization

Particles collected during flood event B were individually photographed along with a scale rule using a stereomicroscope (Leica MZ16) equipped with a digital camera (DP20, Olympus, Japan) and weighed (AT21 Comparator, Mettler Toledo, d = 0.001 mg). Particles weighing less than 0.001 mg were considered as null weight. The largest particle axis (length, L), the orthogonal largest axis (height, H), the perimeter, and the area were measured using ImageJ (Rasband, 1997). Using their pictures, particles were classified into five morphological categories: line, film, fragment, pellet, and sphere (de Carvalho et al., 2021c; Gündoğdu et al., 2018). Lines were used to denominate thin elongated items, with cylindrical shape and one dimension significantly greater than the other two. They differed from fibres mainly due to their larger thickness (de Carvalho et al., 2021c; Free et al., 2014; Marrone et al., 2021). Fragments denominated pieces of thick plastics of irregular shape with all three dimensions comparable, while films presented a thickness significantly lower than the other two dimensions. Pellets were three-dimensional items of a non-rounded shape, while spheres presented a rounded shape, with every point on its surface having the same distance from its centre (Hartmann et al., 2019; Zobkov et al., 2020). An example of each category is displayed in SI Fig. 2a and at de Carvalho et al., 2021c. Through the analysis of at least 30 pictures for each morphology, we estimate an average width (W) for particles of the same morphological category (SI Fig. 2b). For lines, the width was considered equal to their height, for films and fragments, the width was estimated as 0.08 μm and 0.33 μm, respectively. Pellet had their width considered as half of the length and a sphere's width was considered as the average between length and height (Bagheri et al., 2015; Sneed and Robert, 1958). Width estimates were used to calculate a sphericity descriptor

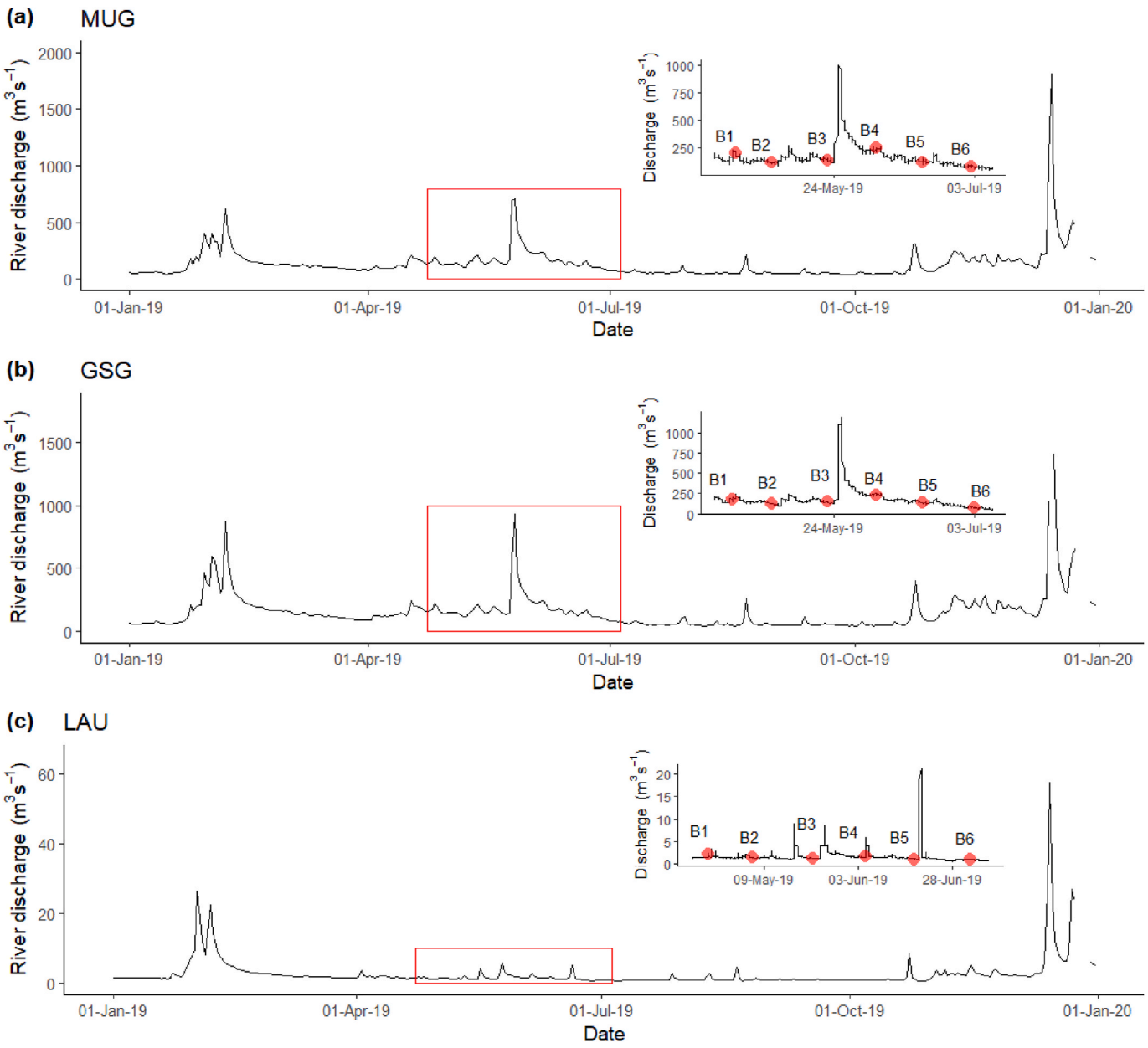

Fig. 2. River discharge (daily average in the main plot, $m^3\ s^{-1}$) in 2019 at (a) Portet-sur-Garonne (Muret, MUG) and (b) Verdun-sur-Garonne (Gagnac, GSG), in the Garonne river, and (c) in the Hers river (Launaget, LAU). The upright plot of river discharge (daily fluctuations, $m^3\ s^{-1}$) displays the six sampling events (B1 – B6, red dots) for each site. Data were obtained from HydroFrance. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

according to the formula (Kooi and Koelmans, 2019; Krumbein, 1941):

$$\text{Sphericity} = \left(\frac{W^{*}H}{L^{2}}\right)^{1/3}$$

A sphericity value close to 1 represents a spherical particle and a small sphericity value a film-like particle.

Each particle was analyzed through attenuated total reflectance Fourier-transformed infrared spectroscope (ATR-FTIR) equipped with a diamond crystal (Nicolet 6700, Thermo Fisher Scientific). The spectrum was acquired with a resolution of 4 cm^{-1} over the wavenumber range of 400–4000 cm^{-1}, through the application of at least 8 scans (de Carvalho et al., 2021c). The crystal was cleaned with ethanol prior to the analysis of each particle and background was collected at each set of eight particles. The ATR correction function available at OMNIC software was applied to each spectrum, which was then compared to available commercial and open access libraries (OMNIC Software, Thermo Fisher Scientific, and OpenSpecy (Cowger et al., 2020), respectively). A minimum match of 70% was used as the threshold to assign a composition to the particle. 78.5% of particles obtained in flood B were microplastics and belonged to the following categories: polyethylene (PE), polystyrene (PS), polypropylene (PP), polydienes, tire and bitumen MP particles (TBMP), and alkyd resins (mainly polyolefin-based, lubrifiants and waxes). The last two categories were considered as microplastic following recent recommendations (Hartmann et al., 2019; Leads and Weinstein, 2019; "Polymer Database," 2020). Only data from these particles were considered for further analysis.

2.5. Quality control

Although risks within the size range of microplastics targeted (>700 μm) are low (Bruge et al., 2020), some procedures were applied to avoid

cross-contamination. During field sampling, all the equipment was rinsed with river water. In the laboratory, all material was rinsed with distilled water and ethanol that were previously filtered through 8 μm polyethesulfone membranes (Sterlitech, EUA). Metal and glassware were used whenever possible and rinsed with ethanol. All the procedure was performed under a fume hood and recipients remained covered with aluminium foil. A cotton lab coat and nitrile gloves were always worn, and work surfaces were cleaned with ethanol prior to each manipulation. Despite the use of polyamide mesh during sampling and sample processing, no polyamide particles were found in this study.

2.6. Statistical analysis

2.6.1. Microplastic concentration

Regarding the first objective, particles concentration was calculated as number of particles per volume of filtered water. Filtered water was calculated using the frame area of the sampling device, which was corrected by the water level at each sampling, and the flow estimated by the flowmeter. For the event A, we considered the total amount of particles collected (particles m^{-3}), whilst only microplastics were considered for event B (MP m^{-3}). The interaction between sampling sites and sampling events on microplastic concentration (log-transformed) was tested using linear mixed effect models (lmm) with replicates as random factor. Independent models were applied for each flood event. To investigate the drivers of changes in microplastic concentration across sampling events, a similar model was used to test the interaction between sampling sites and river discharge. Models were simplified when interactions were not significant.

2.6.2. Microplastic characteristics

Microplastic characteristics (numerical: length, height, area, perimeter, weight, sphericity, and categorical: colour and composition) of microplastics collected during sampling event B were summarized using a factorial analysis of mixed data (FAMD) (Pagès, 2004). This multivariate approach allows to account for the exclusive variance in microplastic properties, originating new variables (called principal components - PC). The first five PC were chosen to be interpreted. PC1 was strongly correlated (correlation >0.7) with the variables area, height, perimeter, and length. PC2 was mostly correlated with microplastic sphericity (correlation = −0.66), while PC3 was correlated with microplastics weight (correlation >0.59). PC4 showed the highest correlation for the variables colour and composition ($r^2 > 0.55$), while PC5 was only correlated with microplastic colour ($r^2 = 0.62$). Therefore, PC1 to PC4 were selected to represent the main variance in microplastic properties, presenting eigenvalues of 3.92, 1.61, 1.22, 1.17 and accounting for 26.17% 10.7%, 8.15%, and 7.8% of the total variance, respectively. Microplastics were then analyzed considering their coordinates in these new axes (PC1 to PC4), instead of individually analyzing each variable. The interaction between sampling sites (MUG and GSG) and flood (presence and absence) in microplastic coordinates values was tested using linear mixed-effect models (lmm), considering replicates as random factor. To further investigate the drivers of changes in PC1 to PC4, a similar model was applied to test the interaction between sampling sites and river discharge. If no interaction occurred, models were simplified.

2.6.3. Changes in infrared spectra of polyethylene microplastics

Polyethylene (PE) was the polymer composing most of the particles collected during flood episode B (650 out of 1580 microplastics collected, SI Table 3). For this reason, MP of PE composition (PE-MP) were chosen to have their ATR-FTIR spectrum analyzed. Given the absence of a defined flood episode in LAU, only PE collected in the main stream, i.e. sites MUG and GSG, were considered (71 particles). Changes in the ATR-FTIR spectra of PE-MP were evaluated through principal component analysis (PCA). First, spectra were rounded to unit, preprocessed through baseline correction, normalized by the sum, and scaled using pareto scaling (Jung et al., 2018; Kedzierski et al., 2019; Liland, 2015; R Core Team, 2019). To reduce the influence of the variance in spectral bands inherent to polyethylene related to methylene vibrations, only absorbance bands presented in wavenumber ranges 800–1200, 1500–1900, and 3000-3400 cm^{-1} were selected. PCA was performed with absorbance data at each wavenumber, thus considered as a variable (total of 1050 wavenumbers). Instead of studying selected wavenumbers, multivariate analysis allows to synthesize the main variance in the data into new variables. The interaction between sampling sites and flood in explaining the variation in microplastic new variables was tested using linear mixed-effect models (lmm), with replicates as random factor. To further investigate the drivers of changes in microplastic new variables related to infrared spectra, a similar model was applied to test the interaction between sampling sites and river discharge. If no interaction occurred, models were simplified.

Specifically, for the analysis of changes in microplastic characteristics and infrared spectra profile, sampling events during flood B in sites MUG and GSG were classified as “presence” or “absence” of flood. The sampling event right after the discharge peak (event B4, Fig. 2a and b) was classified as “presence of flood”, and sampling events B1, B2, B3, B5, and B6 were classified as “absence of flood” (Fig. 2).

All analyses were performed using R software v. 4.0.4 (R Core Team, 2019). Data were plotted through package *ggplot2*. (Wickham, 2016). In boxplots, the lower and upper hinges correspond to the first and third quartiles. The upper whisker extends from the hinge to the largest value no further than 1.5 * IQR from the hinge (where IQR is the inter-quartile range or distance between the first and third quartiles). Linear mixed-effects models were performed using the package *lme4* v.1.1–26 (Bates et al., 2015). Significant levels of mixed-effects models were obtained using the ‘Anova’ function in the package *car* v. 3.0–10 (Fox and Weisberg, 2019). Assumptions of linearity and homogeneity of variances on residuals from all models were checked visually. The function emmeans from package *emmeans* v. 1.7.2 (Lenth, 2022) allowed the estimation of marginal means with the purpose of pairwise comparison. FAMD and PCA were performed through the package *FactoMineR* v.2.4 (Lê et al., 2008) while graphs were generated through package *Factoextra* v.1.0.7 (Kassambara, 2015). Baseline correction of infrared spectra was performed with the ‘baseline’ function from package *baseline* v. 1.3–1 (lambda = 4, hwi = 50, it = 10, int = 740, method = ’fillPeaks’) (Liland, 2015), while pareto scaling was performed with ‘scaling’ function from package *MetabolAnalyze* v.1.3.1 (Gift et al., 2010).

3. Results

A total of 581 particles and 1580 microplastics were collected during sampling events A and B, respectively, in the three sampling sites. The distribution of particles collected per sampling site and sampling event is available in SI Tables 1 and 2 Also, all measured microplastic characteristics (quantitative and qualitative variables) are displayed in SI Table 3.

3.1. Increased microplastic concentration during a flood

During flood A, particles concentration in the upstream site MUG was nearly 9 times greater at sampling event A2 (0.10 particles m^{-3} ± 0.06 SD) than at event A4 (0.01 particles m^{-3} ± 0.01 SD). In the downstream site GSG, the same increase in microplastic concentration occurred at sampling event A3 (0.79 MP m^{-3} ± 0.79 SD) compared to A4 (0.09 MP m^{-3} ± 0.05 SD) (SI Fig. 3a). During flood B, microplastic concentration reached a peak of 0.10 MP m^{-3} (± 0.13 SD) in MUG and 0.79 MP m^{-3} (± 0.34 SD) in GSG at sampling event B4, considered as a flood. Compared to the average microplastic concentration in the absence of flood, this was nearly 5 times higher (Fig. 3). The average microplastic concentration in the tributary LAU was higher than the highest concentration in the main flow (1.22 MP m^{-3} ± 0.49 SD).

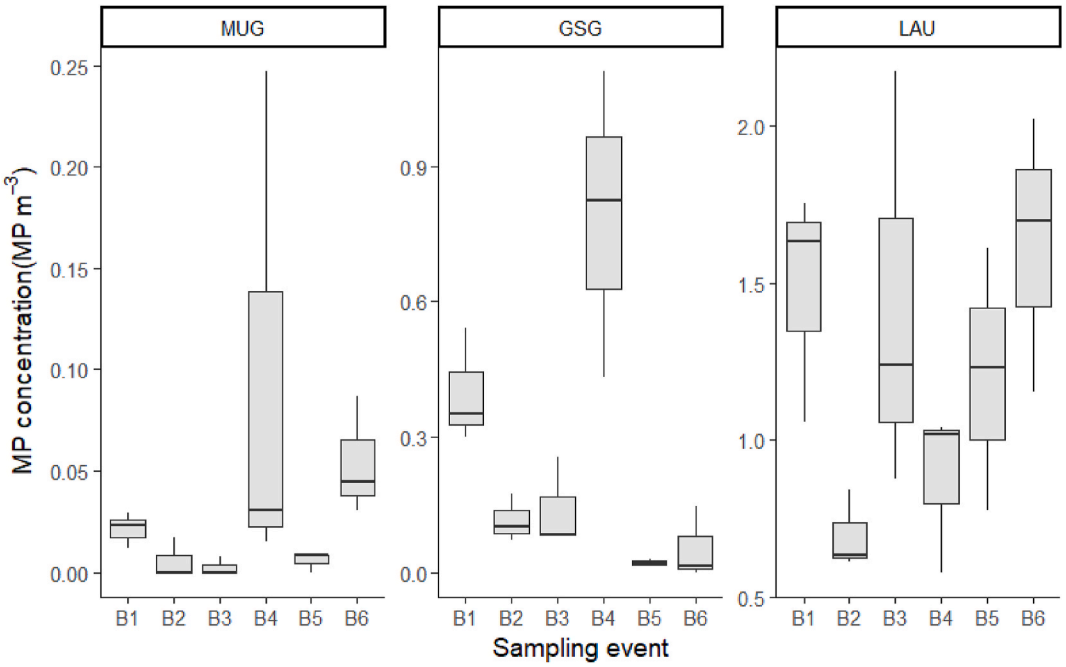

Fig. 3. Microplastic concentration (MP m^{-3}) during flood B in the upstream site MUG, the downstream site GSG and the tributary LAU.

During sampling events, microplastic concentration was significantly smaller at sampling event B2 than B6 for this tributary (lmm, χ^2 = 25.507, p = 0.020) (Fig. 3).

A significant interaction was observed between sampling events and sampling sites in explaining the microplastic concentration (lmm, χ^2 = 7.920, p = 0.048, for flood A and χ^2 = 38.186, p < 0.001, for flood B) (SI Fig. 3a and Fig. 3a and b, respectively). Also, the interaction between river discharge and sampling sites in explaining microplastic concentration was significant for both floods (lmm, χ^2 = 4.138, p = 0.042, for flood A and χ^2 = 20.101, p < 0.001, for flood B). Specifically, increased river discharge had a stronger effect on microplastic concentration in GSG than MUG in both sampling events (SI FIg. 3b and Fig. 4a). No significant relationship was found between microplastic concentration and river discharge in LAU (Fig. 4b).

3.2. *Variation in microplastic characteristics*

The new components of the multivariate analysis were interpreted and PC 1 was better represented by the height, area, and perimeter of microplastics ($\cos^2$ values > 0.6), therefore called "microplastic dimension". Bigger particles presented higher coordinate values in this axis, which also corresponded to white polystyrene particles (higher values) (SI Fig. 4a and SI Fig. 5a). PC2 and PC3 were representative of microplastic sphericity and weight, respectively. PC4 better represented

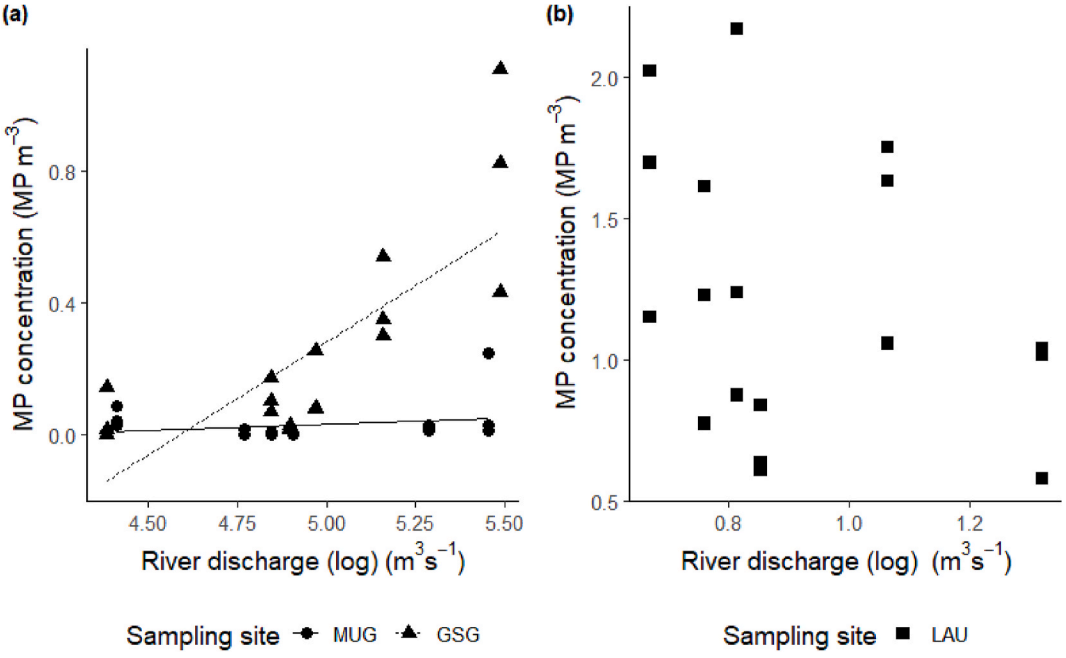

Fig. 4. Relationship between microplastic concentration (MP m^{-3}) and river discharge (log-transformed, m^3 s^{-1}) in (a) the upstream site MUG (circles) and the downstream GSG (triangles) and (b) the tributary LAU (squares).

the remaining microplastic characteristics, colour and composition. At this axis, black particles of polypropylene and other polymeric composition presented the hightes coordinate values, while polyethylene of diverse colours presented smallest values (SI Fig. 4b and SI Fig. 5b).

In both sites, the dimension of microplastic particles (PC1) significantly varied during a flood (MUG: lmm, $\chi^2 = 4.398$, $p = 0.036$ and GSG: lmm, $\chi^2 = 4.603$, $p = 0.032$) (Fig. 5a), with the prevalence of larger particles in the presence of flood. This increase was driven by river discharge in the downstream site (lmm, $\chi^2 = 8.824$, $p = 0.003$). The sphericity and weight of particles (PC2 and PC3) were not affected by the presence of flood and did not vary between sampling sites. Particles colours and composition (PC4) did not vary in upstream site MUG, but presented significantly smaller values during the flood in downstream site GSG (lmm, $\chi^2 = 10.402$, $p = 0.001$) (Fig. 5b). Smaller values in PC4 mostly represent polyethylene microplastics and a greater diversity of colours (SI Fig. 4b). A significant interaction between river discharge and sampling sites in explaining the variation on PC4 was observed (lmm, $\chi^2 = 5.832$, $p = 0.016$). Specifically, the increase in river discharge was negatively correlated with particles values in PC4 axis in GSG, but positively correlated with axis values in MUG.

Microplastics dimension, sphericity and weight (PC1, 2, and 3, respectively) significantly varied in tributary LAU during sampling events, however, no variation was found in microplastic colour and composition (PC4) (SI Fig. 6). Microplastic dimension was significantly smaller at sampling event B2 than B1 and B3 (lmm, $\chi^2 = 16.969$, $p < 0.051$) (SI Fig. 6a), while microplastic sphericity was significantly higher at B5 than B1 and B3 (lmm, $\chi^2 = 11.856$, $p < 0.04$) (SI Fig. 6b). Microplastic weight was significantly higher at samplint event B6 than in all other sampling events (lmm, $\chi^2 = 28.273$, $p < 0.023$) (SI Fig. 6c). Still, no significant relationship was observed between these components (PC 1, 2, 3, and 4) and river discharge.

3.3. Chemical changes in polyethylene microplastics

The first two principal components from PCA of infrared spectra of PE-MP presented an eigenvalue of 0.041 and 0.004 and accounted for 71.6% and 8.6% of the total variance, respectively. The first principal component represents absorbance bands in the range of 3336–3345 cm^{-1}, mainly related to the presence of hydroxyl group (Gardette et al., 2013), and was named as "hydroxyl content" axis. The second principal component represents bands around 1715 cm^{-1}, related with carbonyl group, as ketones (1720 cm^{-1}), carboxylic acids (1713 cm^{-1}), esters (1735 cm^{-1}), and lactones (1780 cm^{-1}) (Almond et al., 2020; Gardette et al., 2013; Karlsson et al., 2018), and was named as "carbonyl content" axis.

The hydroxyl content of polyethylene microplastics did not significantly vary during the flood (Fig. 6a). The carbonyl content of particles collected during the flood was significantly higher than in the absence of flood for both sampling sites (MUG: lmm, $\chi^2 = 4.524$, $p = 0.033$ and GSG: lmm, $\chi^2 = 4.314$, $p = 0.038$, Fig. 6b). This increase, however, was significantly different between sampling sites, once a significant interaction occurred between sampling sites and flood in the variation of PE-MP carbonyl content (lmm, $\chi^2 = 5.253$, $p = 0.022$). River discharge was not correlated with microplastic hydroxyl or carbonyl content.

4. Discussion

In the present study, we found strong evidence for the existence of interactive effects between floods and urbanization on microplastic pollution. Specifically, our results highlight that the increase in microplastic concentration during flood episodes was stronger in the site affected by urbanization (directly downstream an urban area) and driven by river discharge. Microplastic size significantly varied during the flood both upstream and downstream the urban area, with larger particles in periods of higher discharge. However, changes in the

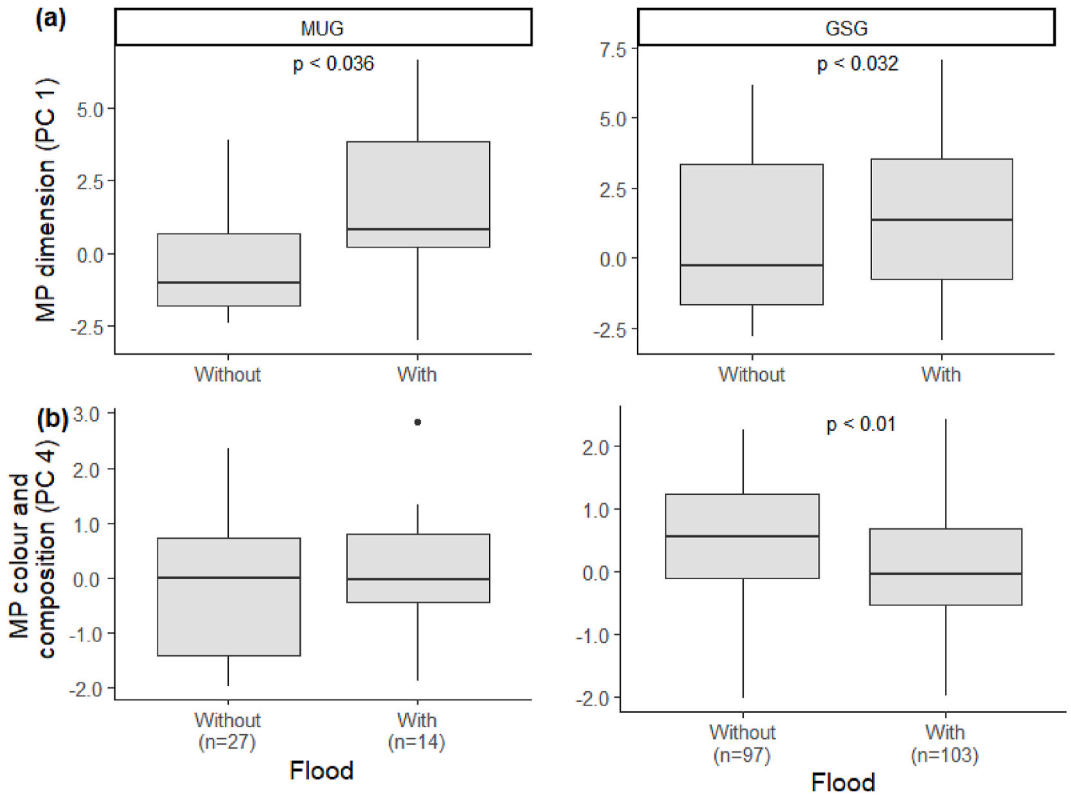

Fig. 5. Microplastic (a) dimension (PC1) and (b) colour and composition (PC4) in the absence or presence of flood in the upstream site MUG (left) and downstream site GSG (right). Significant differences ($p < 0.05$) are displayed in each case.

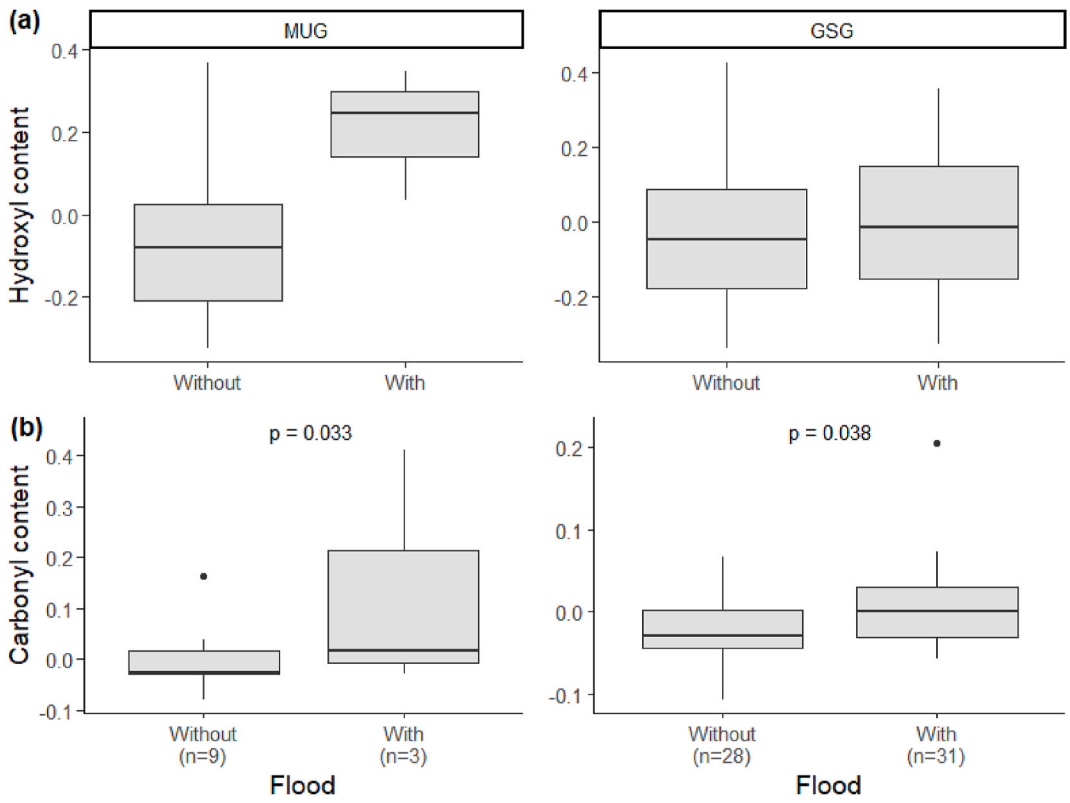

Fig. 6. Polyethylene microplastic (a) hydroxyl and (b) carbonyl contents in the absence or presence of a flood in the upstream site MUG (left) and downstream site GSG (right). Significant differences ($p < 0.05$) are displayed in each case.

distribution of microplastic colours and composition were observed only downstream, mainly representing an increase in the polyethylene type. River discharge had opposite effects on microplastic qualitative profile upstream and downstream the urban area. Finally, polyethylene microplastics collected during the flood presented a significantly higher carbonyl content than the ones collected in the absence of flood.

Microplastic concentration in the downstream site was always higher than in the upstream of the urban area and significantly increased during the flood episodes. There is no information in the literature regarding the time interval following a flood episode that sustains the changes in microplastic concentration on the water surface and these changes might be dependent on the flood intensity and duration. It is important to notice that an even higher peak of microplastic concentration could have occurred between the river discharge peak (May 26th' 2019) and the sampling event B4 (June 05th' 2019) on the main stream. Our findings show that microplastic concentration on the water surface was still elevated 10 days after the peak of river discharge. For the tributary Hers, there was no peak on microplastic concentration, and this concentration was not related to river discharge. Additional studies are needed to understand the existence of a river discharge threshold to observe changes in microplastic pollution.

The increase in microplastic concentration with increasing river discharge was stronger at the downstream site. Three distinct and non-exclusive mechanisms could explain these findings: (i) the indirect microplastic inputs from tributaries, (ii) the remobilization from river beds and banks, and (iii) the direct inputs into the main stream, related to catchment land use. The river discharge in the tributary sampled did not follow the same pattern as in the main river, and the microplastic concentration did not reach a peak during the period sampled. Therefore, it is unlikely that the greater increase on microplastic concentration at the downstream site was caused by tributaries inputs.

The hydrodynamics of microplastics is a complex process, driven by their intrinsic properties and hydrological conditions (Nizzetto et al., 2016). Regarding the latter, a similar profile of river discharge was observed at the two sites on the main stream. Periods of increased flow energy, as in the case of flood events, are known to cause the resuspension of microplastics trapped in riverine sediments, which might be perceived as a long-term sink of microplastic particles (Hurley et al., 2018). Microplastics composed of low-density polymers are commonly found in riverine sediments mainly due to a biofouling process, i.e. colonization of microplastic surface by a biofilm comprising microbial communities, together with the attachment of fouling macro-organisms, that are known to enhance microplastics sinking (Kaiser et al., 2017). Despite the fact that the abundance of microplastics in sediments has been shown to be positively correlated with the level of urbanization (Yang et al., 2021), previous research in the same study area did not find a significant difference between the concentration of microplastics in the sediments of the studied upstream and downstream sites (Garcia et al., 2021). Therefore, the higher increase in microplastic concentration in the downstream site was considered mainly driven by the urban area, as also recently described (Napper et al., 2021). A previous study comparing an urban and a rural catchment highlighted that plastic concentration only increased with river discharge in the urban catchment (Wagner et al., 2019). The higher proportion of impervious area in urban catchments, together with increased anthropogenic activity, contribute to surface runoff and consequently, higher microplastic inputs into the stream (Calianno et al., 2013; Cheung et al., 2019; Kaiser et al., 2021). The microplastic flux to streams, however, might be locally controlled by natural barriers, and the type and extension of river banks vegetation might influence microplastic retention (Delorme et al., 2021). The time spent by plastic debris on land along a river might, in fact, exceed their time within the water and a period of flood can mobilize this accumulated pollutant (Christensen et al., 2020; Tramoy et al., 2019). Further studies are required to determine the role of the near-stream process in regulating microplastic pollution dynamics in streams and their interaction with the catchment-scale process.

Studies about the effects of microplastic on animal and human health are still in their infancy. Due to the impossibility of considering all available combinations of microplastic properties (Bucci et al., 2020; Latchere et al., 2021), such studies are currently not representative of the particles found in the environment. In this study, efforts were made to account for the diversity of microplastics in the environment and to further quantify their spatial and temporal changes. In order to explain the complexity of microplastic particles and the high correlation between their characteristics (de Carvalho et al., 2021a; Rochman et al., 2019; Waldman and Rillig, 2020), eight microplastic properties were measured and resumed through a factorial analysis approach. During the flood, our results showed that larger particles overall prevailed on the water surface. This finding is likely explained by the need for higher water flow energy to mobilize larger particles, and by their higher rise velocity compared to smaller particles (Cheung et al., 2019; Christensen et al., 2020; Kooi et al., 2016). Further laboratory experiments integrating these interacting factors are needed. The input of white polystyrene particles, mainly in foam type, from an urban agglomeration into a stream has been previously described (de Carvalho et al., 2021a; Mani and Burkhardt-Holm, 2019), and this seems to be intensified during a flood episode. We found that the flood episode had an opposite effet on the microplastic qualitative profile at the upstream and downstream sites. Polyethylene particles of diverse colours prevail during the flood at the downstream site, while such profile was not noticed at the upstream site. Polyethylene is greatly used in disposable items and single-use materials, such as packaging, which incidence is correlated with anthropogenic activity (PlasticsEurope, 2020). Although the absence of data regarding colour distribution in plastic production, it is reasonable to expect that an increased diversification of colour types is associated with a greater diversity of sources. The overall profile of microplastics varied between sampling events on the tributary sampled, but no patterns emerged and no drivers were determined. Also, there was no correlation between microplastic properties and the tributary discharge, and these variations were assumed to be related to the intense urbanization, and diverse microplastic input, in the respective catchment (de Carvalho et al., 2021b). 'Hot spots' and 'hot moments' of microplastic pollution represent not only an increased concentration but also a distinct profile that should be taken into account in risk assessment studies. This study highlights the interaction between spatial and temporal variation in explaining the overall changes in microplastic profile, but their implications to freshwater ecosystems functioning remain to be investigated.

The multivariate analysis of infrared spectra allows the identification of the most important wavenumbers responsible for differences between samples (Yun et al., 2019). Based on the analysis of polyethylene ATR-FTIR spectra, the main polymer type, we found that the carbonyl content was significantly greater in particles collected during the flood. Carbonyl groups classically appear when the polymer ages and are considered representative of an oxidative process, providing insights into the extension of microplastic degradation (Andrady, 2011; Karlsson et al., 2018; Kedzierski et al., 2019). The predominance of more oxidized particles during the flood, independently of urbanization, highlights the importance of such events for their input into streams and suggests an important degradation process occurring at a near-stream scale. This is reinforced by recent studies showing an increased degradation in microplastic in dry than in aquatic environments (Tang et al., 2019). Degradation of plastics in the environment results in visible (e.g. discolouration, brittleness) and invisible (e.g. bond scission, formation of new functional groups) effects (Canopoli et al., 2020) that are highly dependent on either the polymer type and the plastic formulation (Fernández-González et al., 2020; Gewert et al., 2015). We decided to analyze the main polymer type found and further studies embracing other polymeric compositions are encouraged. Similarly, the effect of intrinsic plastic components, as formulation additives, in prolonging their environmental lifetime or increasing the susceptibility to oxidation remain to be further investigated (de Carvalho et al., 2021c; Prata et al., 2019; Sait et al., 2021). Future analysis of infrared spectra might consider that the weathering process does not occur uniformly across the microplastic surface and it is recommended to use an average of infrared spectrum acquired at several particle spots. In addition, the biofouling of microplastics might result in additional bands at the infrared spectra corresponding to hydroxyl and carbonyl contents (Maquelin et al., 2002; Zettler et al., 2013). At this study, samples were submitted to a double chemical digestion protocol, likely attenuating this fouling effect that could lead to misinterpretation.

A higher oxidation state of polyethylene microplastics might cause two non-exclusive processes. First, the formation of oxygen-containing functional groups on plastic surface enhances the adsorption of environmental contaminants, such as polychlorinated biphenyls (PCBs), hexachlorocyclohexane (HCHs), and polycyclic aromatic hydrocarbons (PAHs) (Bhagat et al., 2022). Second is the release of residual chemicals from plastic manufacturing, as monomers and additives not chemically bonded to the polymeric chain, that might be favoured under degraded conditions of microplastics (Fred-Ahmadu et al., 2020; Teuten et al., 2009). In addition to the increased oxidation profile, aged microplastics classically present holes and cracks, resulting in an increased surface area and, consequently, increased adsorption of contaminants (Fan et al., 2021). Therefore, polyethylene microplastics collected during the flood present a distinct profile that may pose higher risks to aquatic organisms following ingestion (Beiras et al., 2021; Kwon et al., 2017; Rochman et al., 2014). Oxidation profile is certainly an important factor affecting the fate and behaviour of microplastics in the environment that should be further integrated into experimental protocols.

5. Conclusion

We found that urbanization can strongly interact with river discharge and modulate river microplastic pollution. Changes in microplastic concentration and profile following flood episodes are affected by urbanization, creating 'hot spots' and 'hot moments' of pollution. The input of more oxidized particles into the stream during a flood might be particularly critical to organism's health, as these particles are also expected to contain a higher content of organic contaminants. Unravelling the multiples stress factors generated by microplastic pollution, in space and time, but also within a microplastic particle, contribute to elucidating the complexity of this pollution. To better understand the consequences of microplastic pollution on the health of organisms and ecosystems, more realistic risk assessment studies should therefore be performed, integrating these multiple stressors.

Author statement

ARC: Conceptualization; Methodology; Data curation; Formal analysis; Writing – original draft; Writing – review & editing. **LRG**: Methodology; Writing – review & editing. **ATH**: Funding acquisition; Project administration; Resources; Writing – review & editing. **JC**: Conceptualization; Funding acquisition; Investigation; Project administration; Resources; Supervision; Writing – original draft; Writing – review & editing.

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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.

Data availability

Data and data analysis procedure (R scripts) are available at: https://github.com/ardcarvalho/pub_MPflood-vs-urbanization.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.119760.

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