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Urbanization and hydrological conditions drive the spatial and temporal variability of microplastic pollution in the Garonne River

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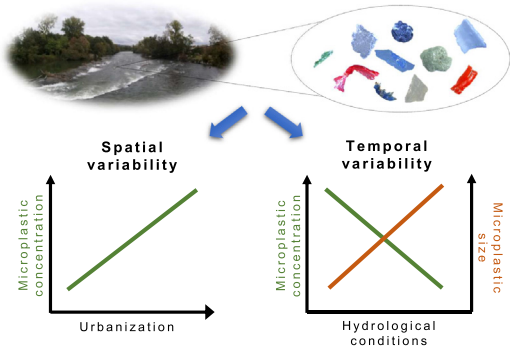
HIGHLIGHTS

- Freshwater microplastic pollution quantification and identification of its drivers
- Microplastic pollution significantly varied between sites and sampling events
- Urbanization increases microplastic pollution
- High concentration and small particles in warm seasons with low discharge

GRAPHICAL ABSTRACT



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ABSTRACT

Microplastic (MP) pollution represents a novel environmental pressure acting on freshwater ecosystems. Improving our understanding of the dynamics of MP pollution in freshwater ecosystems is therefore a prerequisite for managing and limiting this pollution. In this study, we quantified the spatial and temporal variability of MP (size range 700 μm – 5 mm) pollution in surface water in 14 sites located across the Garonne river catchment (Southwestern France, 6 in the main river and 8 tributaries). MP concentration averaged 0.15 particles.m^{-3} (± 0.46 SD) and strongly varied both in space and in time. We found that the spatial variation in MP concentration was driven by urbanization and that the temporal variation in MP concentration and MP size was driven by hydrological conditions, with higher concentrations and smaller particles sizes in warm seasons with low discharge. Polyethylene (44.5%), polystyrene (30.1%) and polypropylene (18.2%) were the main polymers and their proportion did not vary significantly across sampled sites. Particle color was associated with polymer type, with a high proportion of white particles in polystyrene. We also found a significant and negative relationship between MP size and the distance to the source in sites located in the main stream. MP pollution across watershed, from headwater tributaries to lowland rivers, is dynamic, and further studies are needed to improve the resolution of our knowledge of spatial and temporal patterns of MP pollution in freshwater ecosystems.

1. Introduction

Freshwater ecosystems provide countless services to humans, but they are facing multiple disturbances induced by global changes (Vörösmarty et al., 2010). Habitat fragmentation (Morita et al., 2009), water pollution (Couceiro et al., 2007), climate changes (Magnuson

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et al., 1997) and biological invasions (Gallardo et al., 2016) are among the multiple factors threatening freshwater ecosystems and their rich biodiversity. Microplastic (MP) pollution has recently emerged as a novel source of concern with potential effects on freshwater biodiversity and ecosystems that remain to be quantified (Eerkes-Medrano et al., 2015; Eerkes-Medrano and Thompson, 2018). Rivers are at the heart of the dynamic of plastic pollution (Rochman, 2018), notably because they convey 70–80% of the plastics observed in marine ecosystems (Horton et al., 2017). In aquatic environment, plastics undergo a degradation process through mechanical abrasion, photochemical alteration and other weathering processes (Andrady, 2011; Gewert et al., 2015; ter Halle et al., 2017) which leads to the production of MP, i.e. plastic fragments smaller than 5 mm (Arthur et al., 2009; Thompson et al., 2009). In addition, primary MPs (i.e. those not originated by fragmentation of larger debris) often found as cosmetics additives and drug vectors (Cole et al., 2011) can directly enter freshwater ecosystems.

MP pollution is a ubiquitous phenomenon (Lusher et al., 2015; Rochman, 2018; Woodall et al., 2014) and the presence and accumulation of MP in ecosystems represent an important toxicological risk for organisms through direct and indirect ingestion (Prata et al., 2020; Smith et al., 2018). The study of MP properties, such as composition, density, size and color, can not only contribute to elucidate their origins, but also provides insights into the drivers of their consumption by aquatic organisms (Garcia et al., 2021) (Collard et al., 2019; Wang et al., 2019). MP can be ingested by many freshwater consumers taxa, from invertebrates (Windsor et al., 2019) to fish (McNeish et al., 2018; Roch et al., 2019; Slootmaekers et al., 2019) and the consequences of MP consumption on individual are highly variable (Foley et al., 2018). Although there has been a recent increase in the number of studies investigating MP pollution in freshwater ecosystems, improving our understanding of the dynamics of this pollution in these ecosystems is essential (Eerkes-Medrano and Thompson, 2018; Horton et al., 2017).

In rivers, MP pollution varies spatially and is strongly affected by land use (Skalska et al., 2020). Urbanization is a key driver of MP pollution in freshwater ecosystems (Baldwin et al., 2016; Cable et al., 2017; Grbić et al., 2020), and, in highly urbanized areas, MP contamination levels are comparable to those observed in marine environments (Horton et al., 2017). However, our knowledge of the effects of different land use practices on the characteristics of MP pollution remains limited, and MP composition has already been identify as an approach to identification of microplastic sources (Chen et al., 2020). MP pollution can also vary temporally through changes in hydrological and meteorological conditions. Indeed, flood and rainfall can regulate the mobilization of particles previously settled in sediments or on land (Zhang et al., 2017). For instance, MP pollution can be affected by weather conditions and increase after precipitation events (Eo et al., 2019) and several studies have demonstrated a positive correlation between rainfall rates and MP pollution (Cheung et al., 2019; Dris et al., 2015; Wong et al., 2020b; Yonkos et al., 2014). The effects of seasonal variability are more ambiguous, with studies showing either the presence (Han et al., 2020; Wu et al., 2019) or the absence (Mani and Burkhardt-Holm, 2019; Rodrigues et al., 2018) of seasonal patterns. Despite their importance for the development of efficient management strategies on MP pollution in freshwater ecosystems, integrative quantification and characterization of MP pollution and comprehensive analyses of its spatial and temporal drivers are lacking (Lebreton et al., 2017; Li et al., 2020).

The present study aims to fill this gap of knowledge by quantifying the environmental determinants of the spatial and temporal variability of MP pollution (particles with a size range from 700 μm to 5 mm) in surface water of the Garonne river (South-western France). We first quantified the changes in MP concentration across sampling sites and sampling events. We tested the hypothesis that MP concentration was variable spatially and temporally and associated to changes in environmental conditions. The variability in environmental conditions between sampling sites and events was quantified using a multivariate approach. Second, we investigated the spatial and temporal changes in MP composition. We tested the hypothesis that MP composition was different between sampling sites but not between sampling events and correlated with changes in spatial environmental conditions. Third, we explored changes in MP size and hypothesized that MP size varied in time and space, and that this variation was related with changes in environmental conditions. We also tested if there was an overall size difference between MP polymers. Finally, we quantified changes in MP size along the upstream-downstream gradient in the main river.

2. Materials and methods

2.1. Study area and sampling design

This study was performed in the Garonne river catchment, located in southwestern France. The Garonne river is the third largest French river with a mean annual discharge of 630 $m^3.s^{-1}$. It drains about 53.536 km^2 and the main channel flows northwards over 525 km from its source in central Pyrenees in Spain to the Atlantic Ocean nearby Bordeaux, France (Fig. 1). It flows through the large city of Toulouse. Discharge is strongly dependent on snowmelt and is also influenced by precipitations, typically resulting in a flood peak in May–June and a period of low flow from summer to early autumn (Lambs et al., 2009).

Fourteen sampling sites distributed across the Garonne basin were selected to cover the entire spatial heterogeneity in river characteristics and a large gradient of land use (Fig. 1 and Supplementary Table S1). Six sites were located on the main stream of the Garonne river (from upstream to downstream: LBA, LBI, MUG, GSG, CAS and AGE; Fig. 1). Eight sites were located in the downstream part (before flowing into the main stream) of some of the main tributaries of the Garonne river (from upstream to downstream: SLN in the river Neste, RSG in the river Salat, MUL in the river Louge, GRP in the river Ariège, LAU in the river Hers, TOU in the river Touch, GRN in the river Save and LAY in the river Gers). All sites were sampled at four occasions: February 13 to 15, April 23 to 26, July 01 to 04 and October 07 to 09, 2019, to represent seasonal variability in discharge (Supplementary Fig. S1 and Supplementary Table S2). On average, 3 to 5 sites were sampled per day, with a duration of approximately 2 h per site.

MP were sampled by filtering surface water using a Manta trawl (32 cm × 82 cm) equipped with a polyamide net (mesh size of 500 μm) and a removable cod-end with the same mesh size (Faure et al., 2012; Galgani et al., 2013; Hidalgo-Ruz et al., 2012). Each sampling event consisted in attaching the Manta trawl to the bridge guardrail over the river and by immersing it in the fast flowing and deepest parts of each site for approximately 10 min (sampling duration was recorded to the nearest second for each sampling). Sampling of each site was replicated three times at each sampling event with all replicates being performed successively, leading to a total of 168 samples (4 events × 14 sites × 3 replicates). The net entrance was equipped with a mechanical flowmeter (Hydro-Bios, Germany) placed at its center to estimate the volume of filtered water during the sampling duration. The average volume of filtered water was 99.6 m^3 (± 53.7 SD) and ranged from to 4.25 m^3 to 259.10 m^3 depending on the sampling site and the sampling event (Supplementary Table S3). After each sampling, the cod-end content was sieved into a 500 μm mesh using river water and transferred to sealable plastic bags (e.g. Cheung et al., 2019; Wong et al., 2020b). Due to the particle size range considered in the present study, contamination from these bags was very unlikely. Samples were stored in a cooler in the field and stocked at 4 °C in the laboratory before subsequent analyses.

2.2. Sample processing

In the laboratory, the sample processing was composed of five steps, consisting of 1) sieving, 2) chemical digestion, 3) washing/filtration, 4) wet peroxidation and 5) washing/filtration, representing an adaptation

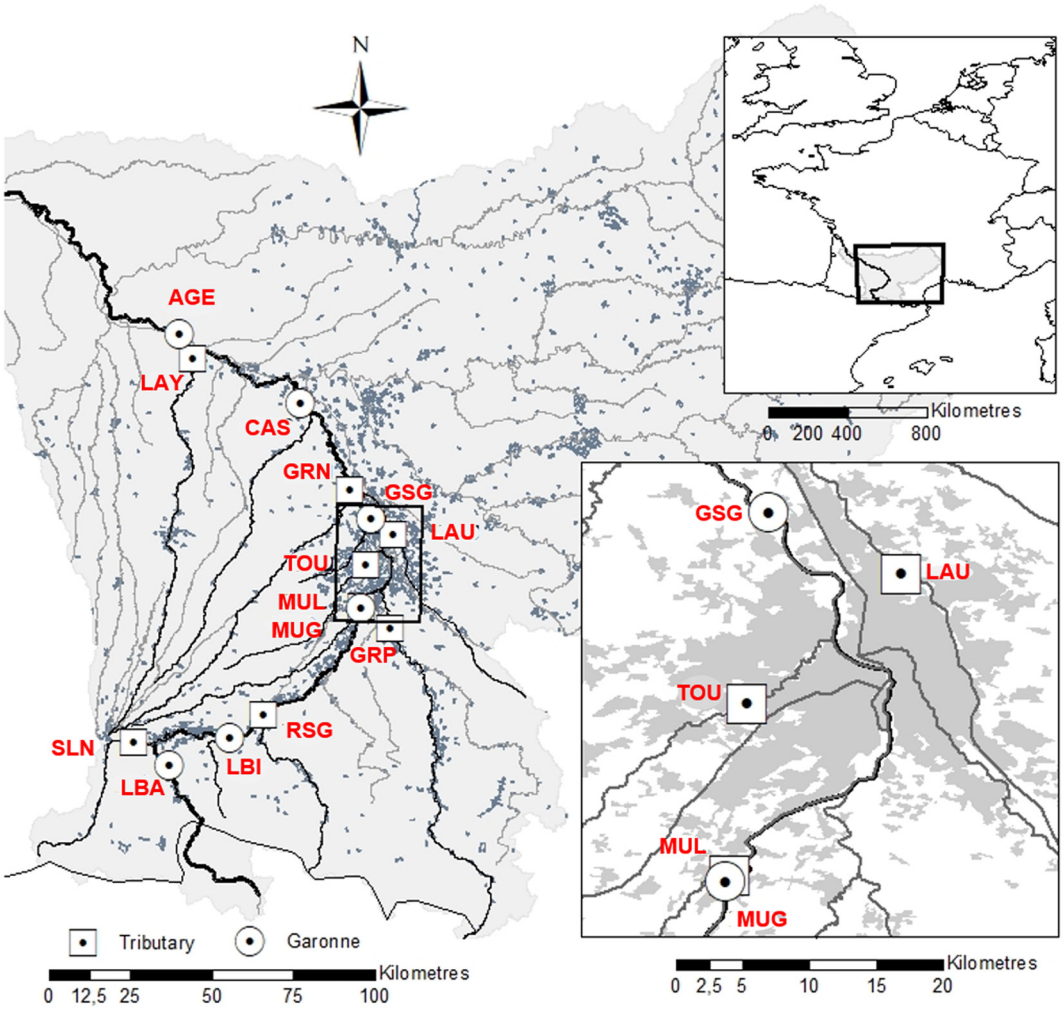

Fig. 1. Map of the study area and localization of the sampling sites.

of existing methods (Dehaut et al., 2016; Hurley et al., 2018; Rodrigues et al., 2018). Samples were first transferred into a sieve (mesh size of 500 μm) to remove large debris (>1 cm) such as tree leaves and branches that were abundantly rinsed with water. The remaining content was transferred into 250 mL glass bottles. Screw caps with aperture (Schott Duran®, DWK Life Sciences, Germany) equipped with polyamide fabric of 500 μm mesh (Nitex®, SEFAR, Switzerland) were used to close the bottles. Chemical digestion was then performed by incubating each sample with enough potassium hydroxide (KOH) (pellets, Sigma-Aldrich, USA) solution 10% (*w*/w) to cover the sample in a water bath (60 °C) for 8 h under intermittent agitation. The sample was filtered through the Nitex® and rinsed with distilled water. A wet peroxidation was carried out by adding enough hydrogen peroxide (H_2O_2) solution (Merck KGaA, Germany) 30% (w/w) to cover the sample and incubating overnight at room temperature (Karlsson et al., 2017). Samples were then finally filtered through the Nitex® and washed with distilled water. The residue content at the Nitex® was stored in petri-dishes at room temperature until further analyses.

2.3. Identification and characterization of microplastic particles

Particles identification was performed using stereomicroscope (Leica MZ 75 and Nikon SMZ 800). Two consecutive inspections of each sample were performed independently by two different operators. The first inspection took an average of 12.6 min (± 11.0 SD) per sample and the second inspection lasted 5.5 min on average (± 3.8 SD). In total, 87% of all particles were detected during the first inspection. All particles ranging from 700 μm (diagonal of the 500 μm mesh net) to 5 mm identified as potentially plastic particles were separated using metallic tweezers and stored in small petri dishes. Each particle was subsequently photographed using a stereomicroscope (Leica MZ16) equipped with a digital camera (DP20, Olympus, Japan) and classified into predefined categories of colors, as black, white, blue, green, grey, red and yellow (Mani and Burkhardt-Holm, 2019) (Fig. 2). The length of each particle were subsequently measured using the ImageJ software (Rasband, 1997), as the length of its longest dimension (Supplementary Fig. S2).

The chemical characterization of each particle was performed by attenuated total reflectance Fourier transformed infrared spectroscopy (ATR-FTIR, Thermo Nicolet 6700, Thermo Fisher Scientific) (Käppler et al., 2016) equipped with a diamond crystal. The ATR crystal was cleaned with ethanol with a background scan prior to analysis of a set of 24 particles. The IR spectra were obtained with a resolution of 4 cm^{-1} over the wavenumber range from 400 to 4000 cm^{-1} applying 8 scans. Each spectrum was compared with the reference spectra of synthetic polymers from commercially available libraries using OMNIC software (Thermo Fisher Scientific). The similarity threshold of 70% was settled for the chemical composition to be assigned to the particle, otherwise it was considered as non-identified (MSFD, 2013). The identified particle was then classified as the polymer type (or polymer artificial additive), based on the Polymer Properties Database (Polymer Database, 2020) when available, or as non-plastic (Supplementary Fig. S3). The final categories of MP composition were: polyethylene (PE), polypropylene (PP), polystyrene (PS), polyester (including

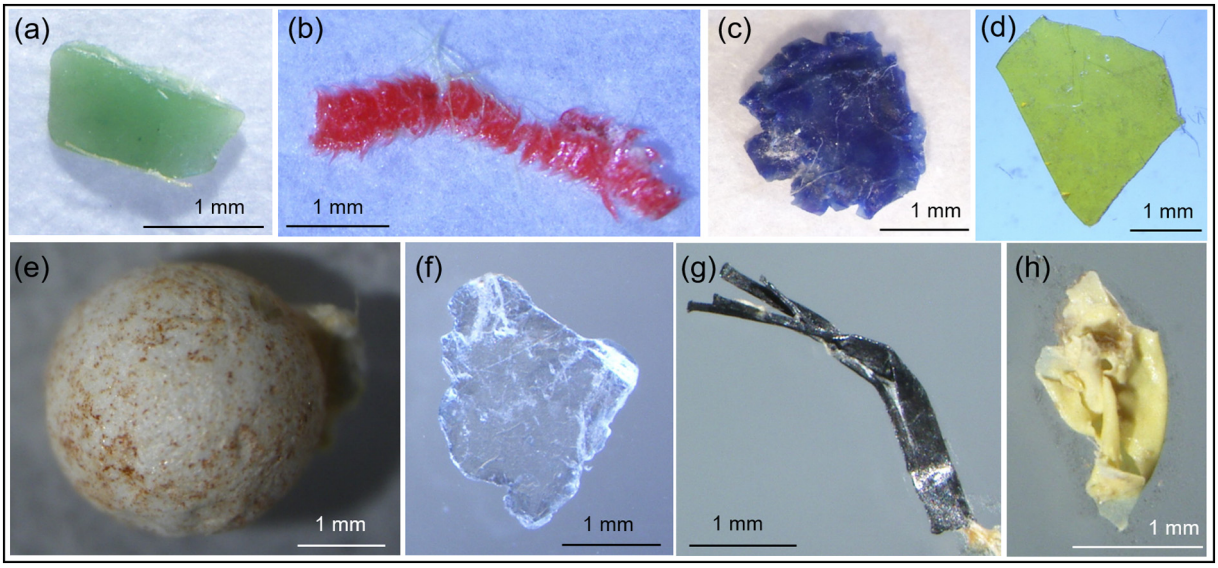

Fig. 2. Examples of microplastics collected in surface water in the Garonne River: (A) green polystyrene; (B) red polyester; (C) blue polyethylene; (D) yellow polyethylene; (E) white polystyrene; (F) white polypropylene; (G) black polypropylene and (H) yellow polyurethane.

polyethylene terephthalate, PET), polyacrylate, polyvinylester, polyamide, polyurethane, polydiene, polysiloxane, polyethersulfone, tire and bitumen MP particles (TBMP) (Järlskog, 2020; Leads and Weinstein, 2019) and artificial additives (considered here as polyolefin-based or alkyd resins, as waxes, oils and coatings lubricants (Hofland, 2012; Song et al., 2014; Su et al., 2020). The last two categories were considered as microplastics (Hartmann et al., 2019), with the latter showing similarities with paint particles (Verschoor et al., 2016). The ATR-FTIR spectra of typical samples and the comparison with a database of spectra are displayed in Supplementary Fig. S4. If the occurrence of a category was less than 5% of the total number of plastics, it was then considered as "other" for further analyses.

2.4. Quality assurance and quality control

The potential effects of the treatment to digest organic matter on particles were measured using raw microplastic pellets. Samples composed of three to five pellets (size ranging from 1 to 5 mm) of the same polymer were analyzed in triplicates and a total of twelve different polymers were tested (Supplementary Table S4). Mass variation and chemical modification can be caused by chemical digestion and high temperatures, resulting in misdetection or incorrect identification of particles. The weight and ATR-FTIR spectra of each particle were obtained before and after the treatment to digest organic matter. Results revealed that this treatment induced no mass variation and no alterations of infrared spectra Supplementary Fig. S5), leading to unmodified match with reference library. Therefore, this protocol was considered as robust for the present study.

To avoid any cross-site contamination, the sampling equipment was rinsed in the river prior to the sampling of each site. In the laboratory, all material was previously rinsed with distilled water and ethanol. Metal and glassware were used whenever possible. All the procedure was performed under a hood and samples recipients remained covered with original caps or aluminum foil. A cotton lab-coat and nitrile gloves were always worn, and work surfaces were cleaned with ethanol. Fibers particles were not included as MP particles considered in this study.

2.5. Environmental conditions

Environmental conditions in each sampling site and at each event were summarized using multivariate analyses based on a series of spatial and temporal descriptors. Environmental parameters related to water characteristics, as temperature and turbidity (NTU – Nephelometric Turbidity Unit), were measured with a DO probe (ProDSS Multiparameter Water Quality Meter, YSI, USA) at each sampling event and for each site (Supplementary Table S2). Daily discharge of each site (except SLN that had no gauge) were obtained from the Agence de l'Eau Adour-Garonne (Hydro Eau France, 2020) (Supplementary Table S2). Daily air temperature and precipitations were obtained from Meteo France (Meteo France, 2020) (Supplementary Table S5). River width was measured at each site using aerial pictures (Géoportail, 2020). A Geographic Information System (ArcGIS v.10.6, ESRI, Redlands, CA, USA) was then used to calculate, for each site, the distance to the Garonne river source, drainage area, land cover (urban and agricultural) and human population. The distance to the Garonne river source (km) was calculated between each sampling site and the source of the Garonne river following the main river bed and the drainage area (km^2) represented the area of land drained in each site. Urban and agricultural land cover (%) was calculated at a predetermined buffer scale of 5 km long with 1 km large upstream of the each sampling site using the Corine Land Cover database (European Environment Agency, 2018). Human population (numbers of inhabitants) was calculated using the same buffer (INSEE, 2018) which described the population in each municipality. Because municipality did not exactly overlap with our buffer, we calculated the percentage of municipalities' area included in the buffer to assess the numbers of inhabitants.

2.6. Statistical analyses

We first conducted two Principal Component Analyses (PCA) to summarize the spatial and temporal variability in environmental conditions and avoid collinearity among variables used to assess the environmental determinants of MP pollution. Regarding environmental variability across sampling sites, 6 variables (namely river width, drainage area, mean yearly discharge, human population, urban land cover and agricultural land cover) were used. The first two axes of the PCA (eigenvalues of 3.06 and 2.31, respectively) represented 89.39% of the total inertia and were selected for subsequent analyses (Fig. 3a). The first axis or principal component (PC)1 was defined as river size as it was strongly associated ($r > 0.60$) with river width, drainage area and mean yearly discharge. This axis discriminated large sites located downstream in the Garonne river with high discharge (e.g. AGE, CAS, GSG) from smaller sites, located upstream in the Garonne river and its tributaries displaying lower discharge (e.g. LBA, GRN, LAY). The second axis (PC2) was defined as the

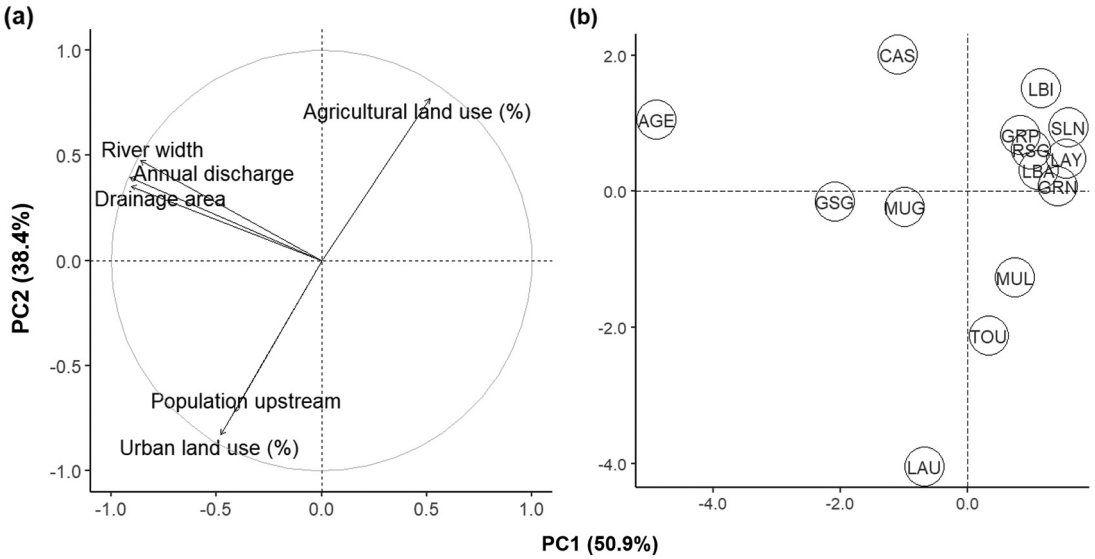

Fig. 3. Summary of environmental conditions on the PCA across sampling sites: (a) correlation circle for spatial variables and (b) distribution of sampling sites along PC1 (river size) and PC2 (urbanization) axes.

level of urbanization as it was strongly associated ($r > 0.60$) with human population density, urban land cover and agricultural land cover. This axis discriminated sites located in an agricultural landscape with low human population density (e.g. LBI, SLN, GRP) from sites with high population density located in highly urbanized area (e.g. LAU, TOU, GSG) (Fig. 3b).

Regarding environmental variability across sampling events, we used 7 variables in the PCA representing the temporal changes in environmental conditions: water temperature, air temperature (day before sampling), precipitations the day before sampling and cumulated across three days before sampling, relative turbidity (calculated as the relative values across the 4 sampling events within each site), relative discharge (calculated as the relative values across the 4 sampling events within each site), and discharge fluctuation (relative change in discharge observed within 3 days before sampling). The first two axes of the PCA (eigenvalues of 3.06 and 2.28, respectively) represented 76.33% of the total inertia and were selected for subsequent analyses (Fig. 4a). The first axis (PC1) represented seasonal hydrological conditions as it was strongly associated ($r > 0.60$) with relative discharge, relative turbidity and air and water temperatures. This axis discriminated sampling events performed in low discharge and turbidity conditions and with high air and water temperatures (e.g. July) from events performed when discharge and turbidity were high, and air and water temperatures were low (e.g. February). The second axis (PC2) was strongly associated ($r > 0.60$) with precipitation that occurred 24 h and 72 h before sampling and changes in discharge, and was therefore defined as weather changes. This axis discriminated sampling events that occurred in dry conditions (e.g. July) from events that occurred with some rainfall and increased stream discharge (e.g. April) (Fig. 4b).

MP concentration was calculated as the number of microplastics particles divided by the volume of filtered water ($MP.m^{-3}$). We used a linear mixed-effects model (lmm) with sampling event or sampling site as a random factor to test if MP concentration (log-transformed) differs between sampling sites or between sampling event, respectively. A similar model was then used to test the effects of spatial environmental conditions (PC axes: river size and urbanization) on MP concentration, with sampling event as random factor. We then tested the effects of temporal

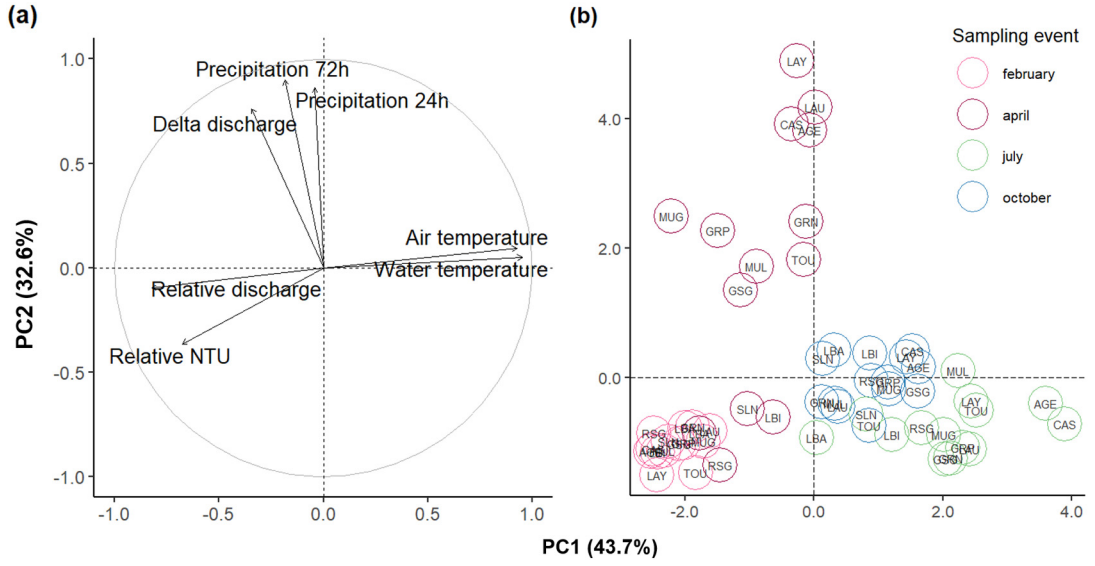

Fig. 4. Summary of environmental conditions on the PCA across sampling events: (a) correlation circle for temporal variables and (b) distribution of sampling events along PC1 (seasonal hydrological conditions) and PC2 (weather changes) axes.

environmental conditions (PC axes: seasonal hydrological conditions and weather changes) on MP concentration, with sampling site as random effect. Fisher Exact test was then used to compare MP colors between MP composition. Spatial and temporal variations in proportion of the three main polymers types (polyethylene, polystyrene, and polypropylene) were tested using generalized mixed-effects models (glmm), considering sampling event and sampling sites as random factors, respectively, using a quasibinomial family. We tested the effects of spatial environmental conditions (PC axes: river size and urbanization) on polymers proportion with sampling event as random factor. Then we tested the effects of temporal environmental conditions (PC axes: seasonal hydrological conditions and weather changes) on polymers proportion, with sampling site as random effect. Linear mixed-effects models with sample code plus sampling event or sampling site as random factor were then used to test for differences in MP size (log-transformed) between sampling sites and sampling events, respectively. Similar models were then used to test the relationship between MP size (log-transformed) and spatial and temporal environmental conditions. The relationship between MP size (log-transformed) and the distance to Garonne source was tested using a linear mixed-effect model with sample code and polymer type as random factors. Finally, a linear mixed-effects model (lmm) was used to test differences in MP size (log-transformed) between polymer types, with sample code as random factor.

All statistical analyses were performed using R v.4.0.2 (R Core Team, 2019) and linear mixed effects models were performed using the package lme4 v.1.1.10 (Battes et al., 2015). Generalized linear mixed-effects models-PQL were performed using the package MASS (Venables et al., 2002). Significant levels of mixed effects models were obtained using the 'Anova' function in the car package (Fox and Weisberg, 2019). All explanatory variables were scaled (mean of zero and standard deviation of one) prior to analyses. Assumptions of linearity and homogeneity of variances on residuals from all models were checked visually. All full models were initially run with two-way interactions. As no interaction was significant, models were simplified.

3. Results

3.1. Spatial and temporal variation of MP concentration

A total of 1887 particles were visually detected. Among them, 1283 were within the studied size range (700 μm to 5 mm) and successfully identified by ATR-FTIR as microplastics (Supplementary Fig. S3). MP concentration averaged 0.15 MP.m^{-3} (± 0.46 SD) and ranged from 0 to 3.4 MP.m^{-3} across all sampled sites and events. There was overall a significant difference in MP concentration between sampling sites (lmm, $\chi^2 = 170.51$, $p < 0.001$). Specifically, we found that MP concentration was significantly higher in LAU than in TOU site, two sites highly urbanized (Supplementary Table S1), that had higher MP concentrations compared to all other sites (post-hoc pairwise comparisons, $p < 0.05$, Fig. 5a). There was a significant effect of the level of urbanization on MP concentration (lmm, $\chi^2 = 108.84$, $p < 0.001$), with MP concentration increasing with urbanization (Supplementary Fig. S6a). There was no significant effect of river size on MP concentration (lmm, $\chi^2 = 3.43$, $p = 0.064$). There was a significant difference in MP concentration between sampling events (lmm, $\chi^2 = 16.53$, $p < 0.001$) with significantly higher MP concentration in July than in February and October (post-hoc pairwise

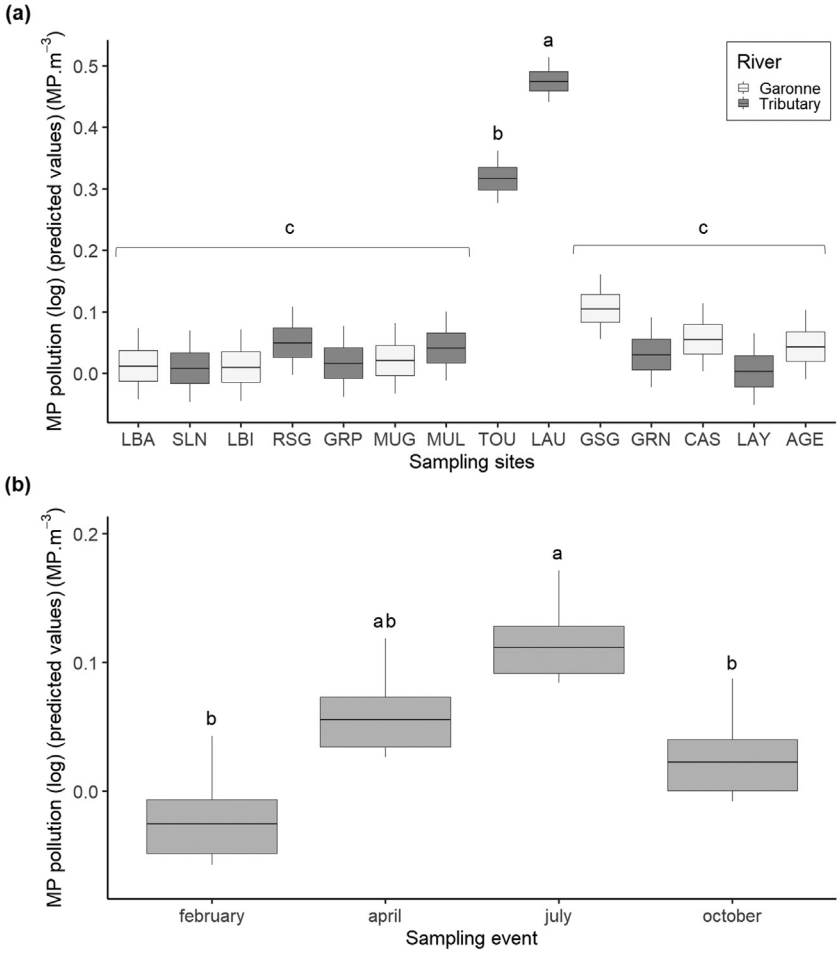

Fig. 5. Microplastic concentration (log-transformed, MP.m^{-3}) across (a) sampling sites (from upstream to downstream), and (b) sampling events. Different letters indicate significant differences ($p < 0.05$).

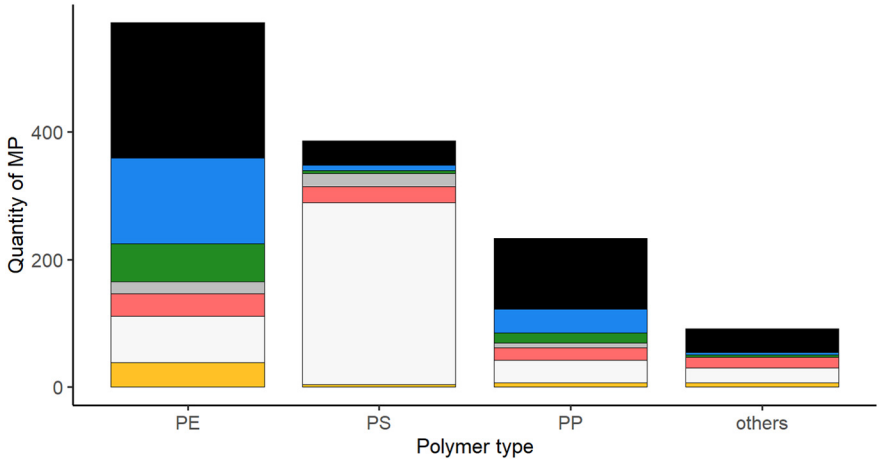

Fig. 6. Distribution of particles colors for each polymer type. Displayed colors represent particles colors (black, blue, green, grey, red, white and yellow, respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

comparisons, $p < 0.05$, Fig. 5b). MP concentration was significantly and positively related to seasonal hydrological conditions with MP concentration increasing in periods of low discharge (lmm, $\chi^2 = 11.20$, $p < 0.001$) (Supplementary Fig. S6b). There was no significant effect of weather changes on MP concentration (lmm, $\chi^2 = 2.56$, $p = 0.109$).

3.2. Spatial and temporal variation of MP composition

Three main types of polymers were collected, namely polyethylene (PE), polystyrene (PS) and polypropylene (PP), representing 44.5%, 30.1% and 18.2% of the total number of particles, respectively (Fig. 6). The other MP particles represented 7.2% of all microplastics (Supplementary Fig.S4). The three main colors of the MP particles were white, black, and blue, and represented 32.4%, 31.1% and 14.3% of particles, respectively. The other MP particles colors were red (7.6%), green (6.5%), yellow (4.5%) and grey (3.6%).

The distribution of particle color significantly differed between polymer types ($p < 0.001$) with a main contribution of the higher proportion of white particles in the PS (37.9%) and smaller proportion of white particles in PE (12.7%) and black particles in PS (10.4%) (Fig. 6).

The proportion of PE, the most abundant polymer, among the sampled MP particles was not significantly different between sampling sites (glmm, $\chi^2 = 12.67$, $p = 0.474$, Supplementary Fig. S7a). There was a significant difference between sampling events (glmm, $\chi^2 = 11.05$, $p = 0.011$, Supplementary Fig. S7b), with a significantly lower proportion of PE measured in October compared to April and July (post-hoc pairwise comparisons, $p < 0.05$). There was no significant relationship between environmental drivers and proportion of PE (Table 1). The proportion of PS was not significantly different between sampling sites (glmm, $\chi^2 = 11.60$, $p = 0.561$, Supplementary Fig. 7c) and between sampling events (glmm, $\chi^2 = 2.87$, $p = 0.411$, Supplementary Fig. 7d). There was no significant effect of environmental variables on the proportion of PS (Table 1). There was no significant difference in the proportion of PP between sampling sites (glmm, $\chi^2 = 19.40$ $p = 0.111$, Supplementary Fig. S7e) and between sampling events (glmm, $\chi^2 = 6.126$, $p = 0.106$, Supplementary Fig. S7f). The proportion of PP was significantly related to river size, with the proportion of PP increasing in larger sites, mainly located more in downstream of the drainage (Table 1). There was no significant effect of the other environmental variables on the proportion of PP (Table 1).

3.3. Spatial and temporal variation of MP size

MP size averaged 2.31 mm (± 1.01 SD). There was no significant difference in MP size distribution between sampling sites (lmm, $\chi^2 = 19.34$, $p > 0.05$) (Fig. 7a), and no significant effect of urbanization and river size on MP size (lmm, $p > 0.05$). There was a significant difference in MP size between sampling events (lmm, $\chi^2 = 12.91$, $p = 0.005$) (Fig. 7b), with larger MP in February compared to other sampling events (post-hoc pairwise comparisons, $p < 0.05$). A significant effect of seasonal hydrological conditions on MP size was observed, with MP size decreasing in low hydrological conditions (lmm, $\chi^2 = 8.64$, $p = 0.003$) (Supplementary Fig. S8). There was a significant difference in MP size between polymer types (lmm, $\chi^2 = 19.38$, $p < 0.05$), with PS being significantly larger than PE and PP (post-hoc test, $p < 0.05$) (Fig. 7c). In the main stream of the Garonne river, MP size significantly decreased when increasing the distance from the Garonne source (lmm, $\chi^2 = 3.909$, $p = 0.048$) (Supplementary Fig. S9).

4. Discussion

The spatial and temporal dynamics of MP pollution in freshwater ecosystems are complex. We demonstrated that spatial variability in MP concentration observed at the catchment level was driven by

Table 1
Results of the mixed effect models testing the effects of environmental conditions of the proportion of the three main polymer types (PE, PS and PP).

	Spatial variability			Temporal variability		
Response	*Parameter*	*t*	*p*	*Parameter*	*t*	*p*
PE proportion	*Urbanization*	1.176	0.241	*Seasonal changes*	−0.014	0.988
	River size	−0.589	0.557	*Weather changes*	−0.664	0.507
	Intercept	−2.484	0.014	*Intercept*	−2.266	0.024
PS proportion	*Urbanization*	1.468	0.144	*Seasonal changes*	−0.119	0.905
	River size	1.929	0.055	*Weather changes*	−0.383	0.702
	Intercept	−10.254	0.000	*Intercept*	−10.605	0.000
PP proportion	*Urbanization*	1.001	0.318	*Seasonal changes*	−0.466	0.642
	River size	2.485	0.014	*Weather changes*	0.898	0.370
	Intercept	−10.225	0.000	*Intercept*	−11.441	0.000

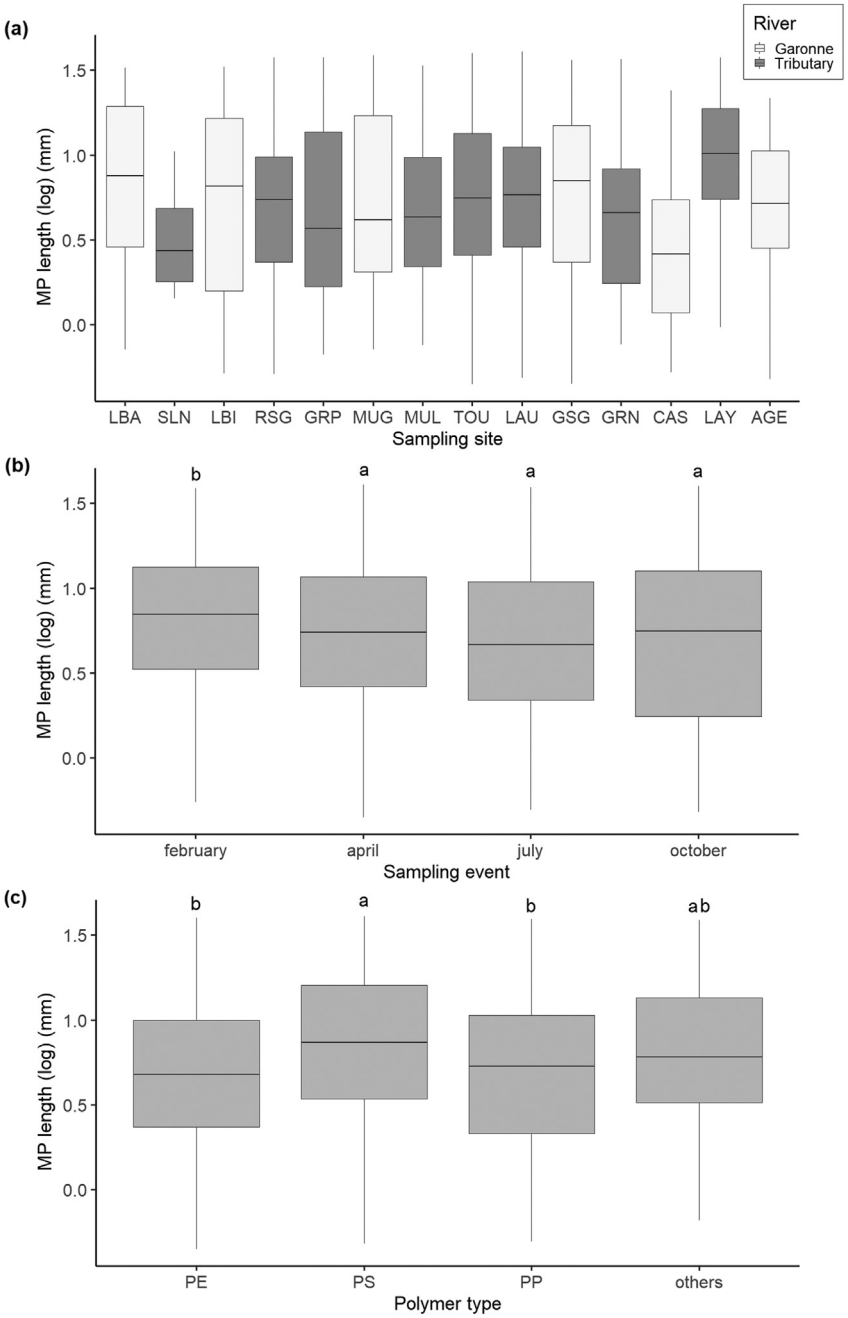

Fig. 7. Microplastic size (log-transformed, mm) between (a) sampling sites, (b) sampling events and (c) polymer type. Different letters indicate significant differences ($p < 0.05$).

urbanization, with MP concentration increasing with urbanization. Temporal variability in MP concentration was strong and driven by seasonal hydrological changes, with higher concentration observed in low flow conditions. We then observed that MP polymers differed in term of color distribution, with higher proportions of white PS and black PE. There was also a temporal variability in the proportion of PE, the most common polymer. The size distribution varied among each polymer, with PS particles being larger. Finally, we found that the temporal variability in MP size was driven by seasonal hydrological changes, with smaller MP encounter in low flow conditions and MP size decreased with the distance to the source only in the main stream of the Garonne River.

4.1. Spatial and temporal variability in MP concentration and its determinants

In general, MP pollution in European rivers is highly variable (Li et al., 2020; Wong et al., 2020a). The mean MP concentration found in this study (0.15 ($\pm$ 0.46) MP.m^{-3}) was within the range of values reported elsewhere (Li et al., 2018), such as in the Rhine catchment (0.04–9.97 MP.m^{-3}) (Mani and Burkhardt-Holm, 2019). However, comparisons between studies are limited by differences in the size range considered and the use of different methodological approaches, from water sampling to extraction of MP particles. MP pollution is also highly variable within catchments, with difference up to a factor of 250 times (Rodrigues et al., 2018). As predicted, a strong spatial variability in MP pollution was observed within the Garonne catchment and driven by urbanization but not by river size. This result is in agreement with previous findings showing that MP concentration was driven by upstream population size rather than watershed size (Christensen et al., 2020), although in the present study a multivariate approach of environmental conditions was applied. We also found that MP concentration displayed a significant temporal variability, with higher levels of MP pollution observed in low flow conditions. Lower MP abundance in

water has previously been associated with weak hydrodynamics conditions in a reservoir and were explained by the reduction in the vertical mixing of MP within the water column (Zhang et al., 2017), with deposition of suspended particles. However, a different mechanism may prevail in our study, probably related with particles size and shape, where low flow conditions result in prevalence of MP in the upper layer of water column, consequently increasing their measured concentration. Therefore, independently of the global flux of MP, MP pollution level in water surface was reduced in high discharge conditions. Weather changes associated to precipitation prior to field sampling did not affect MP concentration. This is consistent with results observed in the Rhine catchment with no relationship between precipitations and MP concentrations (Mani and Burkhardt-Holm, 2019). A relationship between precipitation and MP concentration was observed in Tamsui catchment only in some of the studied rivers (Wong et al., 2020b). While precipitation might move MP from land to the rivers, this increase in MP quantity might not translate into significant changes in concentration due to an increased discharge and changes in suspension-settlement dynamics of particles. Studies are therefore still necessary to elucidate the relationship between precipitations, hydrological conditions and MP concentration to understand how the position within the catchment could modulate this relationship.

4.2. Spatial and temporal variability in MP type

The diversity of polymer types composing MP are driven by a high diversity of input sources, including plastic industries, littering, roads and wastewater effluent (Grbić et al., 2020; Zhang et al., 2017). In the present study, we found that 92.8% of all MP in the Garonne catchment were composed of three main polymers, PE, PS and PP. This finding is very similar to results observed elsewhere (Mao et al., 2020). These polymers are the most common plastics found in the environment (Wong et al., 2020a) and are largely applied in the food packaging, reusable bags, and toys, for example (PlasticsEurope, 2019). Interestingly, this distribution differs from the total European plastic demand, in which these three polymers types represents only 55.4% (PlasticsEurope, 2019), suggesting a difference between the production and this fraction of freshwater MP pollution. The overall low density of these polymers, commonly lower than the water, might explain their presence in surface water (Andrady, 2017; Wong et al., 2020a). However, as these particles are subject to different degradation process while in the environment, which are temporally dynamic and polymer -dependent (Boyle and Örmeci, 2020), their prevalence in water surface might be reduced due to a sedimentation process. For instance, biofouling is known to affect microplastic density, altering their floatability and causing their sedimentation (Karlsson et al., 2018), with studies demonstrating the presence of microplastics composed of low density polymers in river sediments (Van Cauwenberghe et al., 2015). The proportion of PE was higher in low flow conditions, when MP concentration was the highest. Because PE was the main type of polymer observed in the sampled MP, representing almost half of all particles (44.5%), the variation of MP concentration seems to be influenced by the presence of PE particles. We found a significant higher proportion of white PS particles, which is compatible with the higher proportion PS in its foam type (that is, 98% gas and 2% of polystyrene on a volume basis, (Song et al., 2017)) and typically used in packaging or containers (Wang et al., 2019). As most of the PS foam had a spherule shape, their presence in the upper layer of the water column was expected (Van Melkebeke et al., 2020). Moreover, as these particles were weathered only on their surface, a hypothesis of relatively recent emission could be made, as they are expected to easily fragment under mechanical factors (Mani and Burkhardt-Holm, 2019; Song et al., 2017). A comprehensive study of plastic pollution across ecosystem types is essential to identify the potential land sources and transport mechanisms, including the long-term dynamics of MP in the environment.

4.3. Variability in MP size

In streams, MP can be continuously deposited in sediments and resuspended with hydrological dynamics (Rochman and Hoellein, 2020). River banks and floodplains represent a temporal sink of plastics, where larger MP are more easily trapped (Christensen et al., 2020). Contrary to our predictions, there was no spatial variability of MP size across all sampled sites but MP size was affected by seasonal hydrological conditions with smaller MP in low flow conditions. This finding could be caused by the hydrodynamic processes with larger MP needing higher discharge conditions to be resuspended and transported. At the opposite, the proportion of smaller MP particles, that need less force to be resuspended and/or moved, increased in low discharge conditions. Regarding size distribution among polymers types, PS particles were, on average, larger than the PP and PE particles which is in line to the hypothesis of a recent emission of PS particles. The size distribution among polymer types was similar to a previous study (Serranti et al., 2018). Temperature and ultraviolet (UV) radiation play an important role in plastic degradation, at a rate largely depending on its exposure (Christensen et al., 2020; Weinstein et al., 2016) and polymer type, that may also be influenced by the manufacturing process (Julienne et al., 2019). Further studies are needed to better understand the specificities of fragmentation mechanisms within rivers.

Independently of MP composition and sampling event, a negative correlation between MP size and the distance to the Garonne source was observed. Two mutually non-exclusive hypotheses could explain this finding. First, a possible fragmentation of MP particles could occur along the stream (Garvey et al., 2020; Kataoka et al., 2019). Second, and although it was not measured systematically in the present study, water depth differ between sampling sites. Although water surface was always sampled, this fraction represents a proportion of the water column that varies between each sampling site and event. This may have affected the average size of sampled MP particles in surface water because they are not uniformly distributed throughout the water column (Kooi et al., 2017; Kukulka et al., 2012; Law, 2017). MP particles density, sizes and shapes impact their suspension-settlement dynamics (Daily and Hoffman, 2020). Further studies investigating the vertical (Choy et al., 2019; Liu et al., 2020), through the water column, and lateral (Dris et al., 2015) variability in MP pollution are still needed. The temporal variability in both MP concentration and MP size was driven by hydrological conditions. The increase of MP concentration with decreasing MP size was already reported in water and sediments in coastal metropolis (Su et al., 2020). As particle size decreases, they spread over greater distances, and a wider range of organisms are likely to ingest them (Auta et al., 2017). In addition, because MP abundance increases when their size decreases (Morét-Ferguson et al., 2010; Roch et al., 2019), the size limit (>700 μm) used in the present study likely underestimates MP pollution. Because MP size is linked to some of their characteristics, it is important to quantify the characteristics (shape, size and polymer composition) of smaller MPs to fully appreciate how MP pollution is linked to their potential effects on freshwater organisms.

5. Conclusion

This study identified the main environmental drivers of the variability in MP pollution in a large temperate river and revealed that urbanization and hydrology were the main driver of spatial and temporal variability, respectively. We highlight that not only the concentration or polymer type should be quantified in the analysis of MP pollution because variation in MP properties such as size, density and color, can provide a better understanding of the sources and dynamics of this pollution. The dynamic MP pollution across watersheds, from headwater tributaries to lowland

rivers and to its final sink, the marine environment, is complex and multifaceted, and efforts should still be made to improve the spatial and temporal resolution of our understanding of MP pollution in aquatic ecosystems for the management of this pollution (Cable et al., 2017; Rochman, 2018; Skalska et al., 2020).

CRediT authorship contribution statement

Aline Reis de Carvalho: Collected and analyzed samples, Developed analytical method, Conducted laboratory analyses, Drafted the first version of manuscript; **Flavien Garcia**: Collected and analyzed samples, Conducted laboratory analyses; **Louna Riem-Galliano**: Collected and analyzed samples, Conducted laboratory analyses; **Loïc Tudesque**: Collected and analyzed samples, Collected data; **Magali Albignac**: Conducted laboratory analyses; **Alexandra ter Halle**: Designed and supervised the study, Developed analytical method; **Julien Cucherousset**: Designed and supervised the study, Analyzed data, Drafted the first version of manuscript. All authors edited and revised the manuscript.

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

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