Science of the Total Environment 955 (2024) 177113

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Microplastics and microfibers contamination in the Arno River (Central Italy): Impact from urban areas and contribution to the Mediterranean Sea

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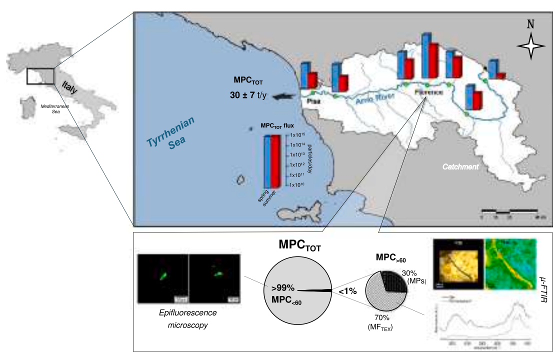
HIGHLIGHTS

- Microparticles (MPC) contamination of the Arno River waters is highlighted.
- μ-FTIR + fluorescence microscopy allows the investigation of a wide MPC size range.
- $MPC_{>60}$ are mainly textile fibers; $MPC_{<60}$ are more abundant and easily mobilised.
- The City of Florence is identified as MPC hotspot.
- Meteorological forcing inland influences MPC contribution from the river to the sea.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Damia Barcelo

Keywords:
Microparticles flux
Natural-based textile fibers
Microplastics
μ-FTIR
Fluorescence microscopy
Mediterranean Sea tributary

ABSTRACT

Fluvial ecosystems are among the main drivers of microparticles (MPC) in the form of both synthetic polymers (i.e. microplastics; MPs) and natural-based textile fibers (MF_{TEX}) to the seas. A wide dimensional range of MPC (5 to 5000 μm, hereafter MPC_{TOT}) were investigated for the first time in the Arno River waters, one of the principal rivers of Central Italy, crossing a highly anthropized landscape. Fluxes of MPC_{TOT} discharging to the Mediterranean Sea, one the most polluted Sea worldwide, were estimated as well. A specific sampling and analytical protocol was set up to distinguish between microplastics (MPs) and natural-based textile fibers (MF_{TEX}) contribution for MPC larger than 60 μm ($MPC_{>60}$), and investigate MPC smaller than 60 μm ($MPC_{<60}$) as well. Results suggest extreme MPC_{TOT} contamination all along the river (up to 6×10^4 particles/L), strongly driven by $MPC_{<60}$, which account for >99 % of total particles found and whose abundance increases inversely with particle size. The $MPC_{>60}$ fraction (<0.5 % of MPC_{TOT}) highlighted a predominance (76 % of the total) of MF_{TEX} and synthetic polymers microfibers (e.g., PET) suggesting strong contributions from laundry effluents. Specifically, MF_{TEX} represent around 70 % of all $MPC_{>60}$. The metropolitan area of Florence was identified as an MPC_{TOT} hotspot as a consequence of the intense urbanization and possibly of over-tourism phenomenon affecting the city.

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https://doi.org/10.1016/j.scitotenv.2024.177113
Received 25 July 2024; Received in revised form 4 October 2024; Accepted 19 October 2024
Available online 31 October 2024

The Arno River discharges approximately 4.6 × 10^{15} MPC_{TOT} annually to the Mediterranean Sea. Fluxes are highly dependent on the seasonality, with a MPC_{TOT} delivery of 2.4 × 10^{13} particles/day and 1.2 × 10^{12} particles/day during wet and dry season, respectively. The total mass of discharged MPC_{TOT} is estimated at about 29 tons/year (t/y); the $MPC_{>60}$ fraction amounts to about 8 t/y, and MF_{TEX} to about 1 t/y.

1. Introduction

The diffusion of microparticles of anthropogenic origin (MPC) in the marine environment is a highly debated topic, especially with respect to microplastics (MPs), defined as synthetic polymers of <5 mm in diameter (Thompson et al., 2004). Global production of plastics exponentially increased from 2 million metric tons in 1950 to 390.7 million tons in 2021 (PlasticsEurope, 2022), generating a large amount of waste which is conveyed to the environment. Primary MPs (i.e., originally produced MPs) and/or secondary MPs, i.e. those resulting from fragmentation due to deterioration, weathering and photo-degradation of macroplastics used or abandoned in the environment, are encountered ubiquitously on Earth from Arctic regions to seafloors (e.g. Emberson-Marl et al., 2023; Nikhil et al., 2024 and reference therein). Once reduced to small size, MPs can be ingested by organisms, significantly impacting their health and becoming available to humans (Al Mamun et al., 2023).

Frequently associated with MPs there is another type of anthropogenic MPC, represented by microfibers mainly employed in the textile industry. Textile fibers include both natural (e.g. cotton, wool, silk) and synthetic (e.g. polyester, acrylic) products. They are extensively used for clothing, households, and industrial applications (Carr, 2017; Yang et al., 2019; Surana et al., 2024), raising the production to a record 124 million tons in 2023 (Materials Market Report, 2024). World production of synthetic fibers (14 % of the global mass plastic production, Geyer et al., 2017) recently surpassed the demand of natural-based fibers (Acharya et al., 2021). Natural-based textile fibers (MF_{TEX}) are essentially represented by cotton, and regenerated fibers, like viscose and rayon. Many studies indicated that MF_{TEX} are predominant (60–80 % of microfibers) in seas and marine sediments (Acharya et al., 2021; Suaria et al., 2020; Gago et al., 2018). Because cellulose is considered biocompatible and presumably biodegradable, it was mostly overlooked in scientific literature (Acharya et al., 2021). However, MF_{TEX} are exposed to a number of chemicals such as dyes and finishes during the manufacturing process, as well as surface modifications (Athey and Erdle, 2022; Acharya et al., 2021). Therefore, once released in the environment, MF_{TEX} may carry harmful chemicals similar to synthetic microfibers and, in addition, they are sufficiently persistent to undergo long-range transport and accumulate in the environment, where they are ingested by biota (Athey and Erdle, 2022).

Rivers, especially those subject to inland anthropic pressure, are at the focus of the scientific community (e.g. Gao et al., 2024) because they impact key sectors of the seas (e.g., fishing and tourism), from which a large share of the world population derives economic and food sustenance. Oceans globally receive 15–20 % of MPs pollution from inland sources via riverine systems (Lebreton et al., 2017; Schmidt et al., 2017). Therefore, the establishment of reliable MPs fluxes from river basins to the sea is one of the major challenges for the understanding of cycling and impact of plastic litter in the marine environment (Constant et al., 2020). A recent review of MPs in surface water on four rivers of Europe (Rhine, Danube, Elbe, Po) indicates a heterogeneous range between 0 and 30 particles/m^3 (Gao et al., 2024). Estimates of the flux of MPs range from 5.92 tons/year (t/y) for the Rhone (Constant et al., 2020) and 6.15 t/y for the Nile River (Shabaka et al., 2022) up to 532.4 t/y for Danube (comprising mesoplastics; Van der Wal et al., 2015).

The Mediterranean region represents an important area for MPs investigation. It is highly populated, with coastal areas belonging to 21 different countries of Europe, Africa and Asia. Numerous streams and rivers crossing highly anthropized inland areas outflow into the Mediterranean Sea. The Mediterranean Sea is described as one of the most MPs-polluted sea basins in the world (Alessi et al., 2018). Despite holding only 1 % of the world's waters, it concentrates 7 % of all marine MPs (Suaria et al., 2016) and it is considered the sixth greatest marine litter accumulation area, with MPs abundances comparable to those found in large oceanic gyres (Cózar et al., 2015).

There are several studies dealing with MPs transport by rivers (see e.g. the review by Schmidt et al., 2017; Treilles et al., 2022; He et al., 2021), but only a few investigated the watersheds discharging into the Mediterranean Sea (Simon-Sánchez et al., 2019; Constant et al., 2020; Zeri et al., 2021). In Italy, the only available data are in the Po River watershed (Munari et al., 2021; Sbarberi et al., 2024). This study aims to fill this data gap by carrying out a seasonal MPs monitoring in the Arno River, one of the most important and impacted rivers of Central Italy. The main objective was to have information on concentrations and fluxes, as well as on the main shapes, dimensions and polymeric composition of MPs. The study explores what is, to the best of our knowledge, the largest dimensional range of MPC (5–5000 μm) ever considered in studies of riverine waters. Many studies, in fact, tend to ignore the smallest and most abundant fractions, often resulting in serious underestimates of the MPC impact (Filella, 2015; Dris et al., 2018). To explore such a wide size range, a combined protocol of sampling and analysis was set up. Another strength of this study is the investigation of MF_{TEX}, seldom considered in fluvial systems (e.g. Dris et al., 2018). Recognition of MPs and MF_{TEX} was achieved by means of micro-Fourier transform-infrared spectroscopy (μFT-IR), which it is one of the most widely used techniques for identifying polymer types (Vianello et al., 2018; Rocha-Santos and Duarte, 2017).

2. Materials and methods

2.1. Study area

The Arno is a 242 km-long river that flows in the Tuscany region (Central Italy). It springs out in the northern Apennines mountains (Mt. Falterona, 1654 m a.s.l.) and it discharges into the northwestern Mediterranean Sea (Tyrrhenian Sea) with an estuary-type outlet (mean water flow rate, Q_{mean}, of 90 m^3/s). Along its pathway, it is fed by several minor and major tributaries. The Arno's drainage catchment covers a surface of 8228 km^2 and it is characterised by annual mean precipitation between 700 and 900 mm, with values up to 2400 mm in the upper Apennine area (Cortecci et al., 2009). The Arno River runs across four different valleys (Casentino, Upper Valdarno, Middle Valdarno, and Lower Valdarno), defining a prevalent East-to-West flow direction.

The Arno River is a strategic source of domestic-use water and hydroelectric energy (2 dams and 12 power plants under construction) that suffers the anthropic pressure of 2.2 million people living in its catchment area (Autorità di Bacino del Fiume Arno, 2024). Despite the several urban wastewater treatment plants (UWWTPs) installed along the course of the river, treated, partially treated, and untreated wastewaters are discharged in it. Specifically, the first part of the basin is affected by effluents from agricultural and zootechnical activity (Nisi et al., 2005), whereas the second half part endures all the urban stress coming from the metropolitan area of Florence (998,431 inhabitants on 1 January 2021) and the largest industrial textile district of Europe (215 factories), located around the municipality of Prato. Along its downstream segment, the Arno River crosses the city of Pisa and shifts to transitional conditions because of tides and seawater intrusion (Cortecci et al., 2002). Continuous and massive tourist activity is expected to affect the river water quality (e.g., Pásková and Zelenka, 2024), especially in the most attractive cities such as Florence and Pisa.

2.2. Sampling

Two sampling campaigns were conducted in 2022, under different hydrological conditions: the high flow stage was investigated at the beginning of April (water discharge at Florence, $Q_{FL} = 50.0\ m^3/s$), after three days of rainfall spread across the catchment, whereas the low flow sampling was performed in mid-July ($Q_{FL} = 4.50\ m^3/s$), after about two rainless months. Seven strategic sampling sites were chosen across the river main course for the investigation of MPC in river waters (Fig. 1a), from nearby the spring (AR1) to the outlet (AR7). Three sites were selected to investigate the anthropic impact before, within, and after the highly urbanized area of Florence and the textile district of Prato (AR3, AR4, AR5, respectively). Site AR4 was located at the famous “Ponte Vecchio” Bridge in the old town of Florence (Fig. 1b), whereas AR5 was positioned immediately after the confluence of the Arno with the Bisenzio River (Fig. 1), the latter collecting the waters from the Prato textile district. The downstream part of the catchment was investigated at site AR6, before the city of Pisa, and the last site (AR7) was located before the Arno River mouth to evaluate the MPs contribution to the Mediterranean Sea. Due to the extreme proximity to the sea, sampling at the AR7 site was carried out under low tide conditions to reduce marine influence as much as possible (S6, Supplementary material, Fig. S15).

In all sampling sites, waters were collected from the centre of the river at a depth of about 50 cm below the surface. At sites AR4 and AR7 waters from the right and left riverbanks were also investigated to characterise MPC distribution across the river section (Fig. 1b,c).

As pointed out by Campanale et al., 2020, sampling MPC in a riverine system is different from the marine environment, made complex by several factors, such as river morphology, hydrological conditions, and different anthropization of the landscape. This complexity has prompted the development of sampling strategies that are typically site specific, and often represent a compromise among contrasting requirements. As a consequence, MPC studies in riverine systems may be affected by errors and biases, and comparison of the results suffers from the lack of harmonized and standardized protocols. For this study, a specific sampling method was developed to collect almost the whole MPC size range (5 to 5000 μm; hereafter MPC_{TOT}). Specifically, two distinct aliquots containing respectively MPC larger than 60 μm (60–5000 μm; hereafter $MPC_{>60}$) and particles smaller than 60 μm (5–60 μm hereafter $MPC_{<60}$) were sampled as described below.

After preliminary tests, 30 L of water was manually collected at each site using a steel bucket and filtered on-site in a steel tank by employing circular nets (diameter of 20 cm) of 60 μm mesh size. Nets trapping particles were stored in pre-cleaned aluminium boxes. Also, 2 L of the filtered water were recovered in two 1 L glass bottles and employed for the investigations of $MPCs_{<60}$. Samples were preserved in a dark place at 4 °C until laboratory processing. Detailed information about the water sampling method is presented in the supplementary material (S1, Supplementary material, Fig.S1).

Specifically, the nature of MPC was determined for $MPC_{>60}$ (see Section 2.4.3), allowing to distinguish between synthetic polymers (i.e. MPs) and natural-based textile fibers (MF_{TEX}).

2.3. Sample processing

2.3.1. Particles extraction from water samples

In the laboratory, collected water samples were processed differently for $MPC_{>60}$ and $MPC_{<60}$. Microparticles retained by the 60 μm mesh size nets ($MPC_{>60}$) were recovered through repeated pressurised MilliQ®

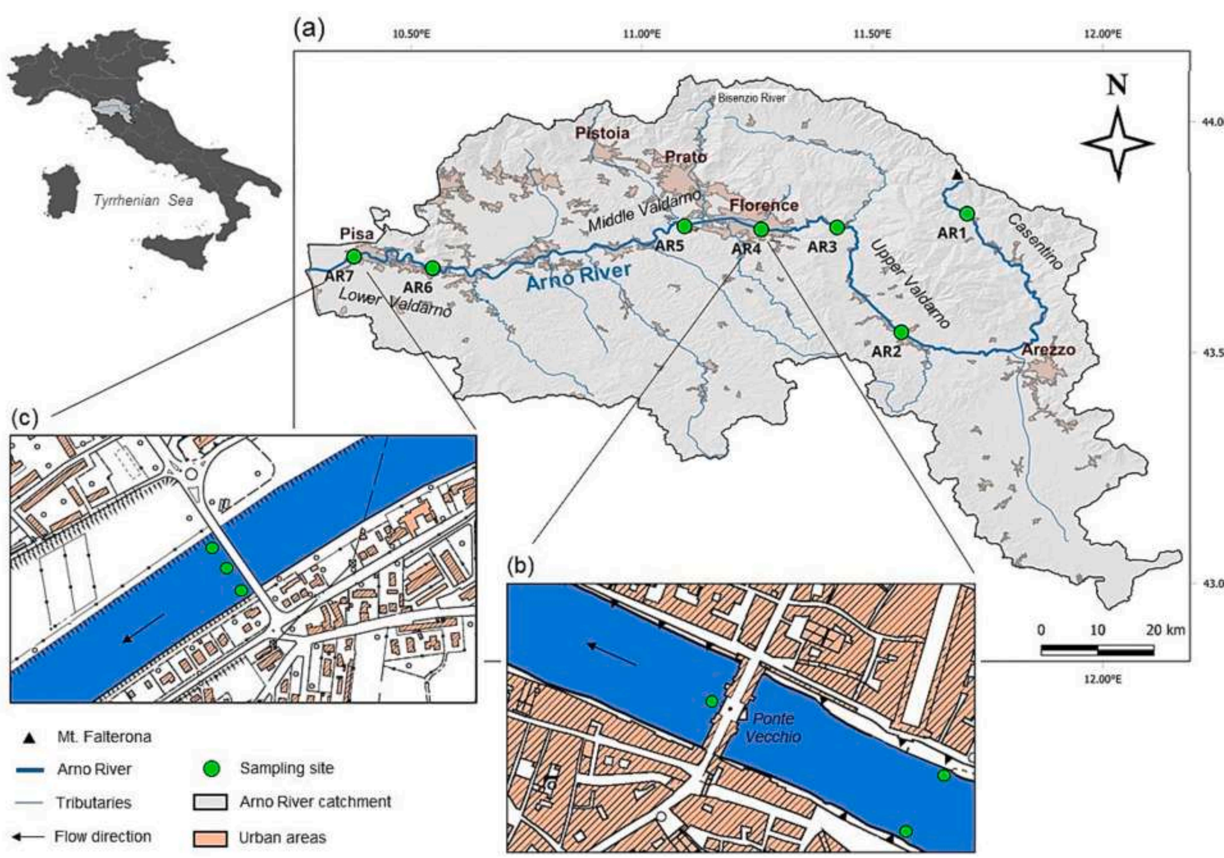

Fig. 1. (a) Map of the Arno River catchment highlighting the location of the seven sampling sites investigated (AR1 to AR7). Detailed maps showing the river centre and riverbanks (left and right) sampling positions at AR4 (b) and AR7 (c) sites are also reported. The black arrows in b) and c) indicate the water flow direction.

water washings of each net with a manual sprayer (max pressure: 3 bar). Flushed water (5 L) on single nets was recovered with a steel funnel, temporarily stored in a glass beaker, and then filtered by a glass Büchner funnel and vacuum pump. For each sample, the 5 L of water were filtered in 5 different pre-baked fiberglass filters (Whatman® GF/A, diameter: 47 mm; pore size: 1.6 μm) to homogeneously spread the suspended particulate load and avoid burial effects of $MPC_{>60}$ (1 L on each filter). The recovery efficiency was calculated and reported in the supplementary material (S2, Supplementary material).

The field collected water (1 L for each sample) passing through the 60 μm mesh was poured through the same vacuum filtration system on four pre-baked fiberglass filters (Whatman® GF/A) for each sample (250 mL of water sample for each filter) to extract the $MPC_{<60}$. The extra litre of water sample collected was used for reproducibility tests (S2, Supplementary material). Filters were carefully transferred in closed fit-filter boxes (diameter: 48 mm), air dried at 40 °C for 24 h and then stored in a dark room until the analyses.

2.4. Identification of MPC in water samples

2.4.1. Visual identification

Microparticles above 60 μm ($MPC_{>60}$) were visually identified with an HD Stereomicroscope (Zeiss© - Discovery V8) equipped with a digital camera (TiEsseLab – GT CAM) and dedicated software (Capture® image analysis). Manual counting was performed on the whole surface of every filter at magnification 40× (size detection limit of ~50 μm). Several criteria were followed to distinguish $MPC_{>60}$ from natural organic matter or minerals: colour, homogeneity, no visible cellular structure, and comparison with images from the literature. The visual window was split into 4 quarters to facilitate the counting; 10 % of the counted particles were chosen, mapped, and classified in terms of shape (fiber, fragment, sphere, films) and colour (black, blue, green, transparent, white, orange, red, yellow, purple, pink, grey), photographed and measured (longest particle dimension). According to the literature, this percentage can be considered a good compromise being sample-representative and time-saving (Faure et al., 2015; Lahens et al., 2018; Rios Mendoza and Balcer, 2019).

To avoid external contamination, each filter was observed keeping the fit-filter box closed.

2.4.2. Epifluorescence microscopy

Water samples containing $MPC_{<60}$ were investigated following a different approach because of the impossibility of selectively distinguishing the smallest particles under the optical microscope. Specifically, a fluorescent staining procedure was performed with a lipophilic dye able to bind to MPs and to MF_{TEX} and to emphasize their presence under epifluorescence microscope. A staining solution of Nile Red (NR) dye (Sigma Aldrich, U.S.A.) was prepared according to the protocol developed by Prata et al., 2019 and added to every filter surface (0.5 mL). The higher affinity of the NR solution with the MPs and MF_{TEX} surface conferred them a differentiated fluorescence at 490 nm compared to minerals in the samples.

Since natural organic matter should present some fluorescence under this staining procedure (Prata et al., 2019), a 0.5 mL of H_2O_2 solution (20 % v/v at 40 °C for 1 h) was pre-added twice to each filter to remove organic material and avoid potential false positives (Akyildiz et al., 2023). In agreement with Tagg et al., 2015 and Masura et al., 2015, this precautionary step was properly carried out under oxidative conditions considered non-destructive and non-altering for MPs polymers, but efficient in decomposing biological matter (Nuelle et al., 2014; Imhof et al., 2012; Wiggin and Holland, 2019). The performed digestion in H_2O_2 is not expected to appreciably digest MF_{TEX} (nor wool; Walawska et al., 2024; Wang et al., 2021; Zeronian and Inglesby, 1995). However, we cannot exclude that some textile fiber was actually destroyed at this step.

Stained MPs or MF_{TEX} particles (S2, Supplementary material, Fig. S2) were then observed under an epifluorescence microscope (Nikon© Eclipse TS2R; 20× objective) equipped with a LED light source (CoolLED pe-300 Ultra) and a CMOS camera (Hamamatsu ORCA-Flash 4.0 V3). The filters containing MPs and MF_{TEX} were sandwiched between a microscope slide and a coverslip. The green LED (wavelength: 490 nm; ex. of the dye: 450–490 nm) was chosen to illuminate the sample and the fluorescence emitted by the stained MPs and MF_{TEX} (dye em.: 515–565 nm) was collected by the CMOS camera. Because of the high number of particles, only ≈ 1.5 % of a single filter surface per sample (≈ 0.14 cm^2) was imaged to speed up the analysis, following the approach of Imhof et al., 2016. In detail, eight squared random spots of 1327 × 1327 $μm^2$ were examined in each filter. Every spot was divided into 4 squares of 663.5 × 663.5 $μm^2$ on which counting, size estimation (max length), and shape characterization of all the fluorescent particles were manually performed. Given the fluorescence properties of stained MPs and MF_{TEX}, particles no smaller than 5 μm were considered. The number of fluorescent particles found in the eight spots of every filter was then extrapolated to the entire filter surface (9.62 cm^2) and related to the sampled volume. Since no indication of polymer type is possible (i.e., MPs or MF_{TEX}), the concentrations (particles/L) should be considered as cumulative of both fractions and were expressed as $MPC_{<60}$ in the following.

2.4.3. μ-FTIR analysis

The 2D imaging-Fourier transformation infrared (FTIR) analysis of the $MPs_{>60}$ was directly carried out on dry fiberglass filters using a Cary 620–670 FTIR microscope, equipped with an FPA (Focal Plane Array) 128 × 128 detector (Agilent Technologies©) and a Cassegrain 15× objective. This experimental setup was selected as it has proven to be highly effective in the identification of plastic particles down to the micron size, even in complex matrices rich with inorganic sediment (Cincinelli et al., 2021). Measurements were carried out in reflectance mode (to avoid saturation from the sample in transmission mode), and background spectra were collected on a gold plate surface before each analysis. Each particle analysis yielded a 2D "tile" map of 700 × 700 $μm^2$ (128 × 128 pixels), where each pixel had a size of 5.5 × 5.5 $μm^2$ and produced an independent spectrum. All the spectra (background and samples) were acquired in the 3900–900 cm^{-1} range, using 128 scans, an open aperture, and a spectral resolution of 8 cm^{-1}. The high number of scans per particle allowed acquisition of clear spectra, despite possible interference of sediment particles on the filter and the need to work in reflection mode. This high number of scans in turn required acquiring maps of individual particles rather than mapping the whole filter.

The detection limit of the detector for synthetic polymers (e.g., polyvinyl alcohol) was recently found to be as low as ca. 0.6 pg/pixel (Mastrangelo et al., 2020). The pixel size of the FPA detector allows the collection of many independent spectra on the polymer microsamples; for instance, >150 independent spectra are typically acquired on a 1 mm long and 10 μm thick fiber in a single sample's "tile" image (700 × 700 $μm^2$). All the spectra were analysed using Agilent Resolution Pro software (Agilent Technologies©). For each polymer, diagnostic bands and the full spectra profile were identified and matched with those of references found in the literature (Canché-Escamilla et al., 2006; Jung et al., 2018), thus allowing assignments.

In the 2D FTIR maps, the intensity of characteristic bands of the investigated polymers was imaged with a chromatic scale of increasing absorbance, as follows: blue < green < yellow < red.

For the polymer classes identified in this study, visible light maps, 2D FTIR maps and spectra are reported in S3, Supplementary material, Fig. S4 to Fig. S13. Details on the identification of MF_{TEX} are given in S3, Supplementary material, Fig. S3.

A representative particle for each morphology class (shape and colour) was selected in each sample for the polymer identification under μ-FTIR (a total of 54 particles for April samples and 52 particles for July).

Once obtained the compositional data by μ-FTIR analysis, concentrations of MPs and MF_{TEX} were separately calculated for each sample by relating the number of particles/fibers visually identified (Section 2.4.1) to the relative abundances of particle/fiber made of synthetic/semi-synthetic polymers and textile cellulose, respectively. Abundances were expressed as particles/L. The total MPC (MPC_{TOT}) in the Arno River waters were calculated as $MPC_{<60} + MPC_{>60}$ (MPs + MF_{TEX}). We emphasize that these estimates are subject to large uncertainties because of extrapolation from small to very large volumes.

2.5. Estimation of MPC fluxes

Flow rates (m^3/s) and hydrometric levels (m) during the two field sampling campaigns were acquired from the SIR database (Regione Toscana; SIR, 2024). At each site, the daily fluxes of MPC_{TOT}, $MPC_{<60}$, MPs and MF_{TEX} (particles/day) were calculated as follows:

$$Flux_{ARn} = (Conc._{ARn} \times Q_{ARn}) \times 86,400$$

where "Conc." indicates the concentrations of MPC_{TOT}, $MPC_{<60}$, MPs or MF_{TEX} (particles/L) in water, "Q" is the water flow rate (L/s), "ARn" is the sampling site, and 86,400 is the number of seconds (s) in 1 day.

Furthermore, at site AR7 and AR4 the daily fluxes were calculated for the river centre and left/right riverbanks site to provide indication about variability among the river section (Table S1, Supplementary material). Finally, the yearly average input (particles/year) to the sea was estimated considering the hydrological conditions and the particle concentrations in water during the investigated months (April and July), as representative of the whole year 2022. The average daily flux between the two seasons was then calculated and extrapolated for 365 days (S5, Supplementary material). This is another source of uncertainty because of the highly erratic variations of the river discharge in response to rain events.

Under the same spatial and temporal considerations, $MPC_{>60}$ (MPs and MF_{TEX}) and $MPC_{<60}$ mass discharges (weight) into the sea were also estimated by calculating and defining the volume and the density of MPC (S5, Supplementary material).

2.6. Quality assurance/quality control (QA/QC)

Field and procedural blanks were run to check potential on-site and laboratory contamination. Blank samples were performed by exposing 60 μm nets next to the collecting site, to assess the MPC airborne deposition introduced by atmospheric fallout and synthetic clothing worn by the sampling staff.

Laboratory blanks simulating every extraction step were run considering (i) the background signal from fiberglass filters, (ii) water used for cleaning equipment (MilliQ and deionised water contained in the manual sprayer), and (iii) reagents (H_2O_2, NR). All the analytical operations were performed under laminar flow fume hood, using plastic-free tools (e.g., aluminium foils, steel tweezers, lab. glassware) previously washed with ultrafiltered MilliQ to minimize the sources of secondary contamination. Baked fiberglass filters were put under the fume cupboard to check potential deposition of air particles during the lab processing.

Sampling and laboratory processing steps were performed wearing yellow coats made of a specific synthetic polymer (polypropylene) and gloves to allow the diagnostic identification of the potential clothing contamination.

Control blanks of water samples contained an average of 16 $MPC_{>60}$ μm and 68 $MPC_{<60}$. Compared to the number of particles found across all samples, this contamination was considered negligible.

Concentrations in the water samples were corrected by subtracting the respective number of MPC on the field and processing blanks.

2.7. Statistics

Statistical analyses were carried out through R software (R Core Team, 2024) to evaluate spatial and temporal variations in concentration and flux. A *t*-test (two-sided, unpaired) was used to check statistically significant differences (p-value <0.05) between consecutive and not consecutive sampling sites. The confidence level of the interval was 0.95 (95 %).

3. Results

3.1. Concentrations of MPC in the Arno River waters

Microparticles of anthropogenic origin were found in all the investigated Arno River water samples.

The abundance (mean ± SD) of MPC_{TOT} in shallow water varied from 4390 ± 1286 (AR7) to 53,006 ± 15,529 particles/L (AR4) in April, and from 1370 ± 401 (AR7) to 56,009 ± 16,410 particles/L (AR4) in July. At every site $MPC_{<60}$ represented >99 to 100 % of the MPC_{TOT} for both seasons (Table S1, Supplementary material), therefore in the following the results of $MPC_{<60}$ in place of MPC_{TOT} are described.

The maximum concentrations of $MPC_{<60}$ were observed at the Ponte Vecchio urban site AR4 (Fig. 2a), followed by a general decrease (p-value <0.05) moving towards downstream sites in both seasons (from 52,996 ± 15,528 particles/L at AR4, to 4371 ± 1281 at AR7 particles/L in April; from 56,001 ± 16,408 particles/L at AR4 to 1366 ± 400 (AR7 particles/L in July). Concentrations of $MPC_{<60}$ showed no statistically significant variations (p-value >0.05) among the river centre and the left/right (L/R) riverbank water at site AR4 and AR7 in both seasons (Fig. 2b, c).

Micro-litter larger than 60 μm (<0.1 % of MPC_{TOT}) at some sites is represented by 100 % MF_{TEX} (Fig. 2a). Concentrations of MF_{TEX} in April varied from 1.4 ± 0.3 (AR1) to 15.7 ± 3.7 particles/L (AR7), and in July from 2.5 ± 0.6 (AR4) to 9.8 ± 2.3 particles/L (AR5).

Concentrations of MPs varied between 4.3 ± 1.0 (AR4) and 3.9 ± 0.9 particles/L (AR7) in April, while no MPs were observed in the first three sites (AR1, AR2, AR3), located upstream Florence (Fig. 2a). In July, MPs ranged between 1.0 ± 0.2 (AR7) and 7.6 ± 1.8 particles/L (AR4). MPs were not found at site AR5.

Similarly to $MPC_{<60}$, MPs showed higher concentrations at the urban site of Florence (AR4). In July, MPs showed an increasing trend along the first part of the Arno River stretch (AR1-AR4) and decreased towards the outlet (Fig. 2a). Concentrations of MPs were higher in the dry season at AR1, AR2, AR3 and AR4 sites, while in the last stretch of the river concentrations in the dry season were lower than in April (AR5, AR6 and AR7 sites).

$MPC_{>60}$ concentrations along the riverbanks of AR4 and AR7 were respectively −50/−49 % (left/right; L/R) and − 70/−84 % (L/R) lower than the river centre (p-value <0.05) in April. In July, these differences became less pronounced (−21/−52 % and − 17 %/−4 % L/R) at AR4 and AR7, respectively) (Fig. 2b, c).

3.2. Characterization of MPC in the Arno River waters

A total of 2238 MPC_{TOT} were characterised for their length. Length distribution did not show significant differences between the two seasons for both the size fractions $MPC_{<60}$ and $MPC_{>60}$ (Fig. 3a, b).

Average $MPC_{<60}$ length was 285 μm, and the majority of particles were 5–15 μm (61–70 %), followed by 16–30 μm (18–30 %), 31–45 μm (6–8 %), and 46–60 μm (3–4 %). The average $MPC_{>60}$ length was 940 μm, and in both seasons the most abundant size fraction was 1001–2000 μm (19–26 %), followed by the 2001–5000 μm (10–14 %), and no significant frequency differences were highlighted between the size classes.

The $MPC_{>60}$ were further characterised by shape, colour, and polymer type. Fibers were the most abundant shape, characterizing around 76 % of $MPC_{>60}$ (79 % of MF_{TEX}; 21 % MPs). Fragments and films

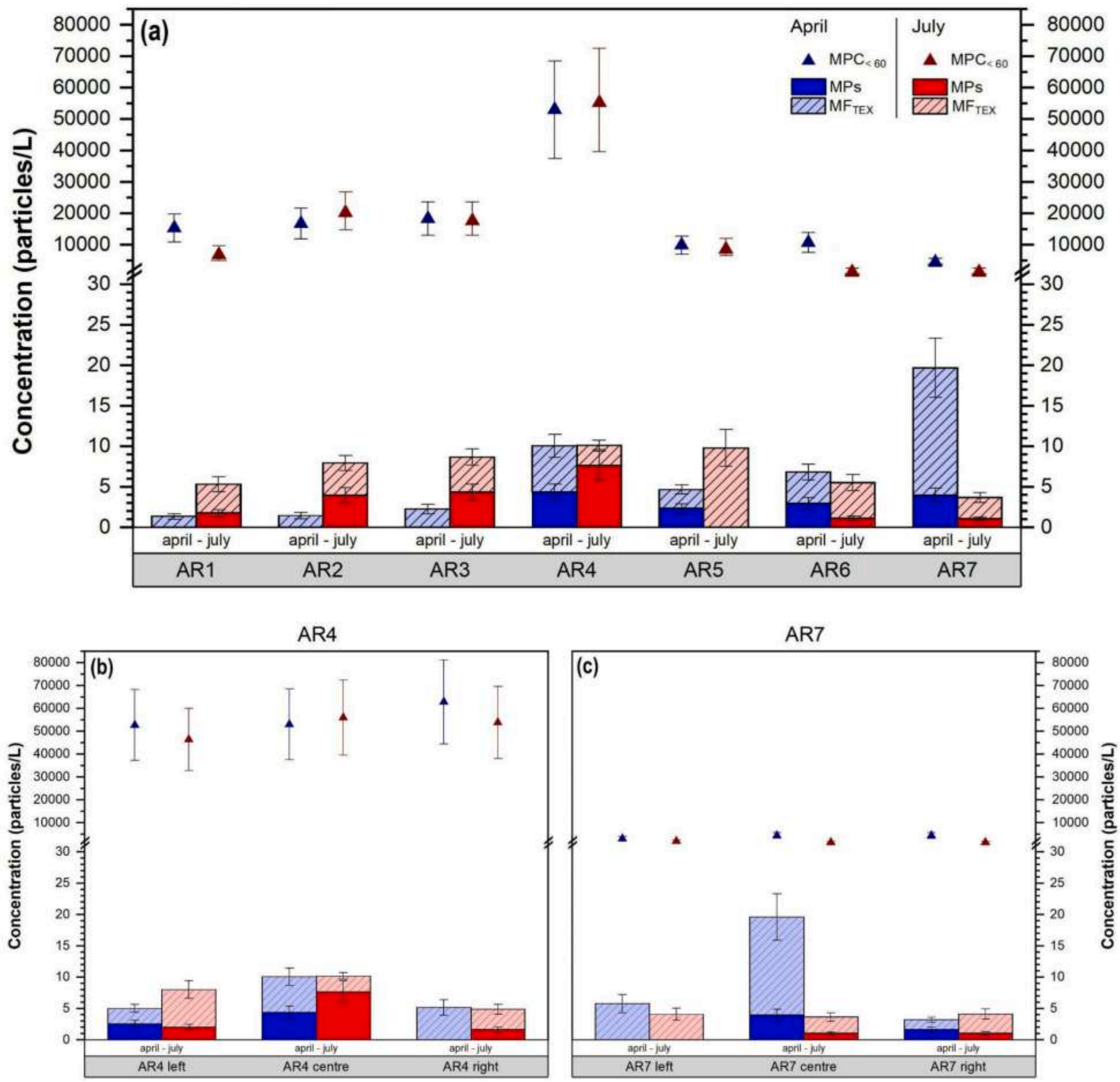

Fig. 2. Concentrations (particles/L) of $MPC_{<60}$ (triangles) and $MPC_{>60}$ as MPs and MF_{TEX} (coloured bars) for the seasons investigated (April and July): a) all the sampling sites. Site AR1 represents the most upstream sampling location, and site AR7 is the most downstream sampling location; b,c) AR4 and AR7 sites, in the centre, and left and right riverbank.

covered the remaining 23 % and 1 %, respectively. Specifically, in April the MPs were dominated by fragments (57 %) and fibers (43 %). On the contrary, MPs fibers were more common (53 %) than fragments (41 %) in July, and also films (6 %) were found (AR4 site) (Fig. 4).

Seven colour classes were observed for MPs. The most common colours were blue and red, each accounting for 23 % of the total, followed by green (19 %), black (16 %), transparent (13 %), yellow (3 %), and purple (3 %). The MF_{TEX} showed eight different colour classes. Blue fibers were ubiquitous and the most abundant, representing 39 % of the total, followed by red (25 %), black (15 %), transparent (9 %), green (7 %), orange (3 %), yellow (1 %), and purple (1 %) (Fig. 4).

Micro–Fourier transform infrared (μ-FTIR) characterization of 106 particles selected from the observed $MPC_{>60}$ allowed the identification of eight MPs polymer classes (4.7 % of the analysed particles could not be identified), as reported in S3, Supplementary material, Fig. S4 to Fig. S13. Most of them were polyethylene terephthalate (PET; 38 %), followed by acrylonitrile butadiene styrene (ABS; 16 %), blends (styrene-acrylates and PP-PET copolymers; 13 %), polyamide (PA; 9 %), polyacrylonitrile (PAN; 9 %), elastomers (neoprene and others; 9 %), polyethylene (PE; 3 %), and poly-methyl-methacrylate (PMMA; 3 %). Elastomers were identified only at sites AR4 and AR7 in July samples. The majority of PET particles (91 %) found along the Arno River showed a fiber morphology and around 50 % of them were observed at the AR4 site (Fig. 5).

Natural-based textile fibers (MF_{TEX}) represented 73 % and 65 % of all the $MPC_{>60}$ detected in April and July, respectively (average of around 70 %).

3.3. *Fluxes of MPC in the Arno River*

The calculated MPC fluxes (MPC_{TOT}, $MPC_{<60}$, MPs and MF_{TEX}), are reported in S4, Supplementary material, Table S2 together with the flow rate measurements (Q; m^3/s) and the hydrometric levels (wl; m a.s.l.) of the Arno River during the sampling campaigns. >99 % of MPC_{TOT} fluxes at all sites is determined by $MCP_{<60}$, due to the predominance of small particles (<60 μm) in all samples (S4, Supplementary material,

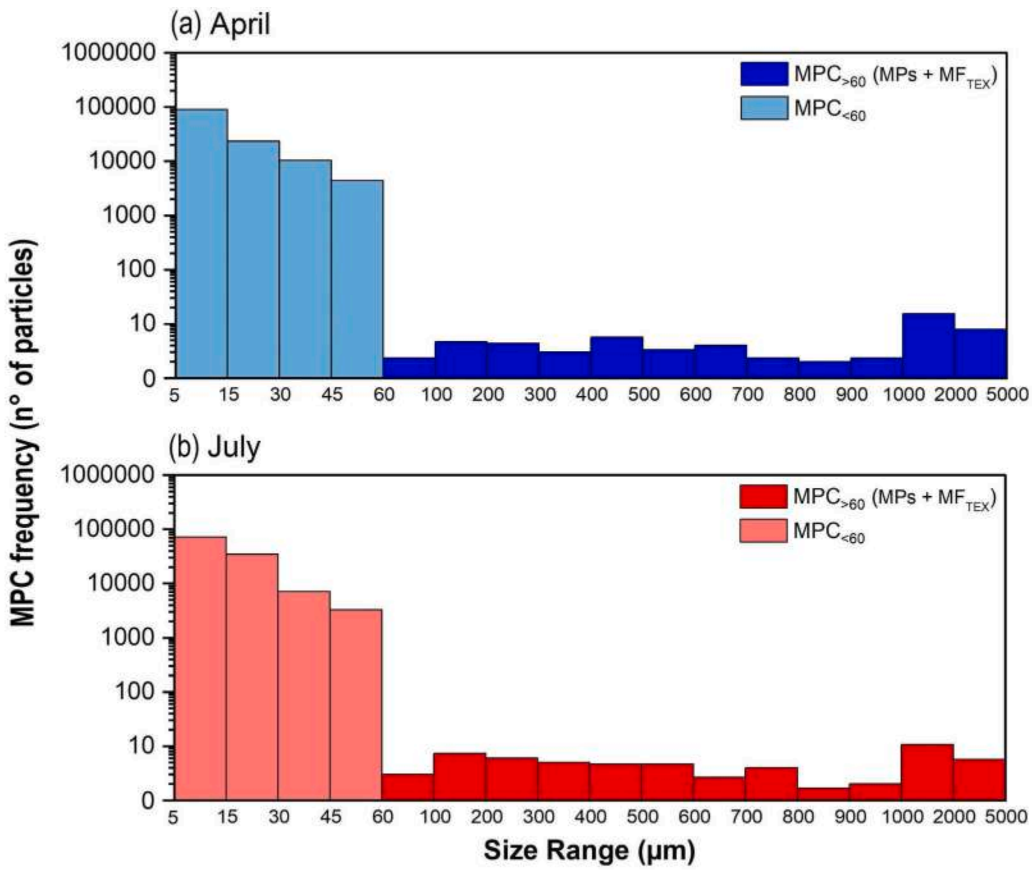

Fig. 3. Size distributions of $MPC_{<60}$ and $MPC_{>60i}$ in shallow water along the Arno River at all sites in (a) April and (b) July. To allow the comparison between fractions, MPC frequencies (log scale) were obtained by normalizing the number of particles sized to the total particles found in the filter surface and reporting the result to 1 L of water.

Table S1). In the following, we report in detail the result of fluxes of $MCP_{<60}$ and $MCP_{>60}$ (MPs and MF_{TEX}) (Fig. 6).

In April daily fluxes (mean ± SD) of $MCP_{<60}$ ranged from a minimum of $1.4 \pm 0.4 \times 10^{12}$ to a maximum of $2.3 \pm 0.7 \times 10^{14}$ particles/day, and from $3.2 \pm 0.9 \times 10^{10}$ to $2.2 \pm 0.6 \times 10^{13}$ particles/day in July. In both seasons the lowest and maximum fluxes were observed at the blank (AR1) and at the Ponte Vecchio (AR4) sites, respectively. Also, in both seasons, the fluxes of $MCP_{<60}$ increased from AR1 to AR4 (p-value <0.05), while they generally decreased or did not show significant variations from A4 up to AR7. Seasonal variability was observed at all sites, with a reduction of one to two orders of magnitude in $MCP_{<60}$ fluxes from the wet (April) to the dry season (July). At the AR7 site, $MCP_{<60}$ discharges into the Mediterranean Sea seasonally varied from $2.7 \pm 0.8 \times 10^{13}$ (April) to $1.0 \pm 0.3 \times 10^{12}$ particles/day (July) (Fig. 6).

Plastic microparticles >60 µm also showed a spatial and seasonal trend. In April, daily fluxes of MPs were constant in the second part of the river stretch, reaching maximum value ($2.4 \pm 0.6 \times 10^{10}$ particles/day) at the outlet site (AR7). At the first three sites (AR1, AR2, AR3), no MPs were observed.

In July, MPs fluxes showed a trend similar to the $MPC_{<60}$, with low daily fluxes at AR1 ($7.6 \pm 1.8 \times 10^{6}$) increasing to a maximum of $3.0 \pm 0.7 \times 10^{9}$ particles/day (AR4) (Fig. 6). At site AR5 no MPs were observed.

The daily fluxes of the MF_{TEX} showed a similar increasing trend in the first three sites, with higher concentrations at AR4 in April ($2.5 \pm 0.6 \times 10^{10}$) than in July ($9.9 \pm 2.3 \times 10^{8}$) and low variability in the last three sites, both in April and July (Table S2).

When not null, the daily fluxes of MPs and MF_{TEX} (i.e. $MPC_{>60}$) were three to four orders of magnitude lower than the $MPC_{<60}$ (Fig. 6) along all the course of the Arno River and in both seasons.

4. Discussion

4.1. Sources of MPC along the Arno River

Microparticle contamination of the Arno River was evaluated through the simultaneous interpretation of MPC concentrations and mass loads from upstream sites to the river outlet.

The ubiquitous presence of plastic micro-litter all along the river defines a non-negligible MPC contamination, dominated 99–100 % by the smallest fraction (<60 µm). In the upper part of the Arno River, supplies of $MPC_{<60}$ were found across the rural and sparsely populated districts of Casentino and Upper Valdarno (Fig. 1). Despite their low anthropogenic landscapes, these areas negatively affected the $MPC_{<60}$ budget of the Arno River waters, as demonstrated by the increasing concentrations (up to 18,303 ± 5363 particles/L) and fluxes, one to two orders of magnitude higher (from 10^{10} to 10^{12} in July and from 10^{12} to 10^{13} in April) moving from the blank site AR1 to AR3. The impact of the urban area of the city of Florence (Middle Valdarno) is highlighted by the marked deterioration of river water quality at the Ponte Vecchio location (AR4), in the historical and highly touristic urban centre of Florence, where an $MPC_{<60}$ peak concentration of $>50 \times 10^{3}$ particles/L was observed in both seasons. Fluxes (central sampling point) concordantly increased up to $2.3 \pm 0.7 \times 10^{14}$ (April) and $2.2 \pm 0.6 \times 10^{13}$ (July) particles/day (Table S2).

After the urban site, $MPC_{<60}$ have a decreasing trend both in concentrations and loads. Sedimentation of $MPC_{<60}$ due to lower riverbed slope gradient, could explain this gradual decrease of $MPC_{<60}$ fluxes along the second part of the catchment. River sediment may thus act as a temporary sink for $MPC_{<60}$, as widely reported in the literature (Castañeda et al., 2014; Nel et al., 2018).

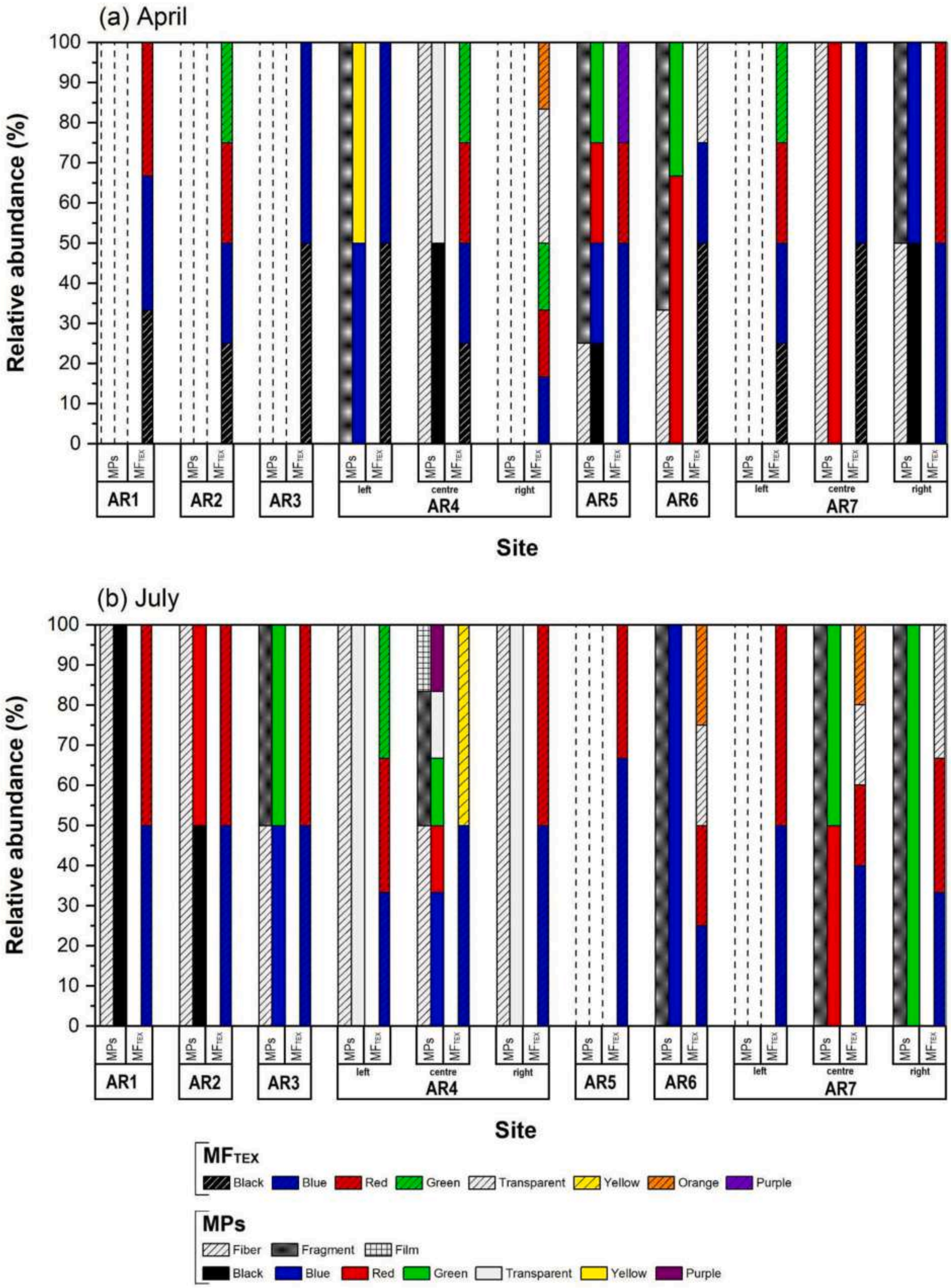

Fig. 4. Relative abundances (%) of shape (fiber, fragment, film) and colour classes for the $MPC_{>60}$ (MPs and MF_{TEX}) along the Arno River in (a) April and (b) July. Dotted bars are reported where no MPs were detected.

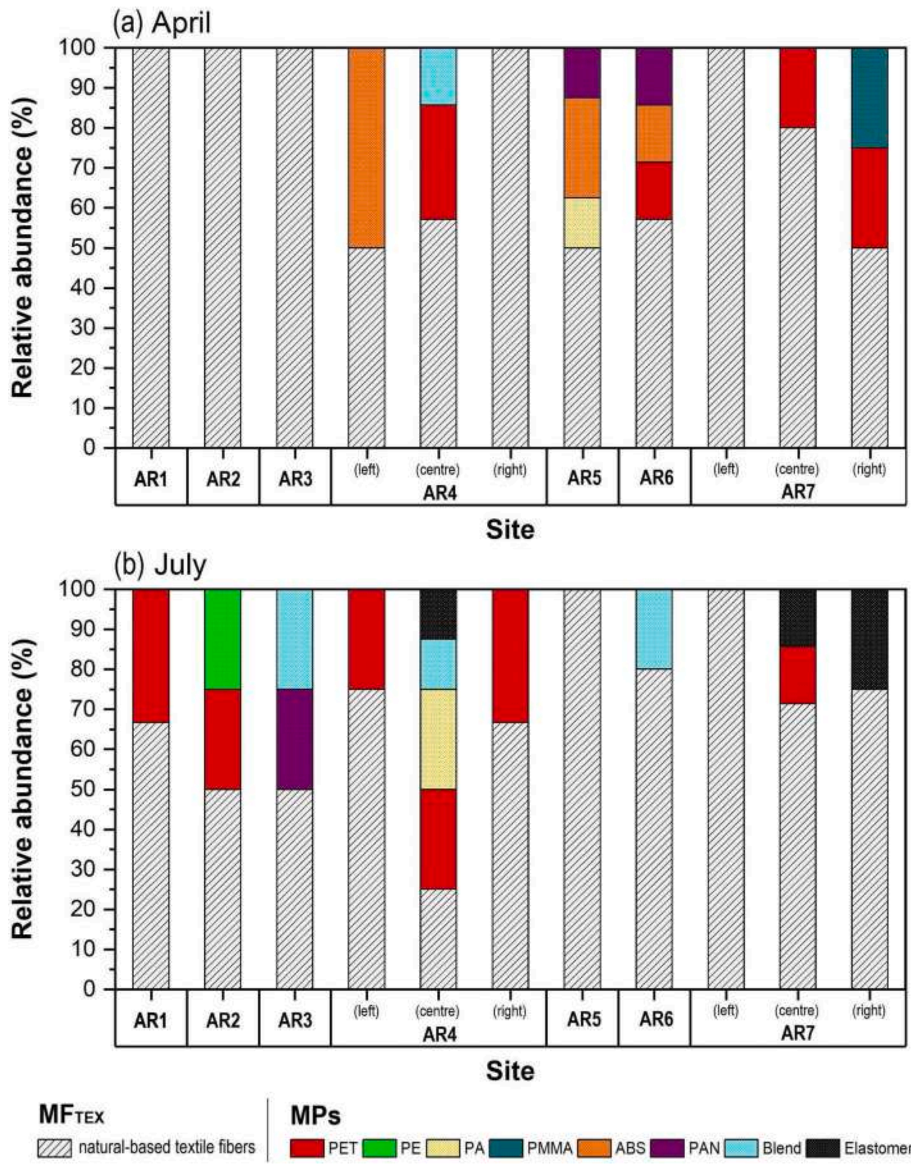

Fig. 5. Relative abundances (%) of natural-based textile fibers (MF_{TEX}) and microplastics polymer classes (MPs) along the Arno River in (a) April and (b) July.

Microplastics and MF_{TEX} fluxes also increase up to three orders of magnitude from the blank to the Ponte Vecchio sites, where they peak to $1.9 \pm 0.4 \times 10^{10}$ and to $2.5 \pm 0.6 \times 10^{10}$ particles/day in April, respectively (Fig. 6).

Considering the trends of concentrations and fluxes found along the Arno River, the city of Florence represents a $MPC_{<60}$, MPs and MF_{TEX} hotspot.

The anthropic impact on the freshwater bodies crossing the urban network of the city of Florence was previously described by Rimondi et al., 2022 in the Mugnone Creek, a tributary of the Arno River and one of the main urban creeks draining the city centre of Florence. The study highlighted a severe MPC contamination (up to 16,000 particles/m^3, including MF_{TEX} particles) in the urban area, especially after rainfall events triggering greater washing of impervious surfaces and favouring micro-litter mobilization processes (up to 1.5×10^9 particles/day transported by creek waters). Despite its minor stream class ($Q_{mean\ 2022} = 1.20$ m^3/s; SIR), the Mugnone Creek can be considered a verified MPC source to the Arno River (Rimondi et al., 2022). A similar role can be inferred for the Bisenzio River ($Q_{mean\ 2022} = 3.10$ m^3/s; SIR), joining the Arno River immediately before the AR5 site, and draining the biggest European industrial textile district of the city of Prato (Fig. 1), although no MPC data is available in the Bisenzio River. Concordantly, MF_{TEX} represent 100 % of the $MPC_{>60}$ flux during summer at AR5 (Table S2), suggesting a contribution of this industrial area to the river. The decreasing trend of $MPC_{<60}$ fluxes observed at the two downstream sites, crossing the city of Pisa (195,000 inhabitants in 2023) and close to the river outlet, could be explained either to i) a not significant anthropic contribution from this urban settlement, or to ii) complex dynamics of transport/deposition control the pattern of MPs and MF_{TEX}. The two explanations are not mutually exclusive, but, as detailed below, we are inclined to give more importance to the second.

The proximity to the river outlet is influenced by estuary transitional dynamics. Estuaries are considered temporary sinks for MPC before reaching the seas (Malli et al., 2022), and represent complex systems where the mixing between fresh and marine waters can cause a dilution (Lam et al., 2020) or enrichment (Zaki et al., 2021) in MPC abundance compared to the continental river stretch. The decreasing fluxes described along the last stretch of the Arno River could be controlled by the occurrence of MPC deposition processes and/or to the marine influence (tide activity and seawater intrusion), recorded >20 km inland (Electric Conductivity, E.C. 1825 μS/cm at AR6 in July), as also found by Cortecci et al., 2002. A similar decreasing gradient of MPs towards the

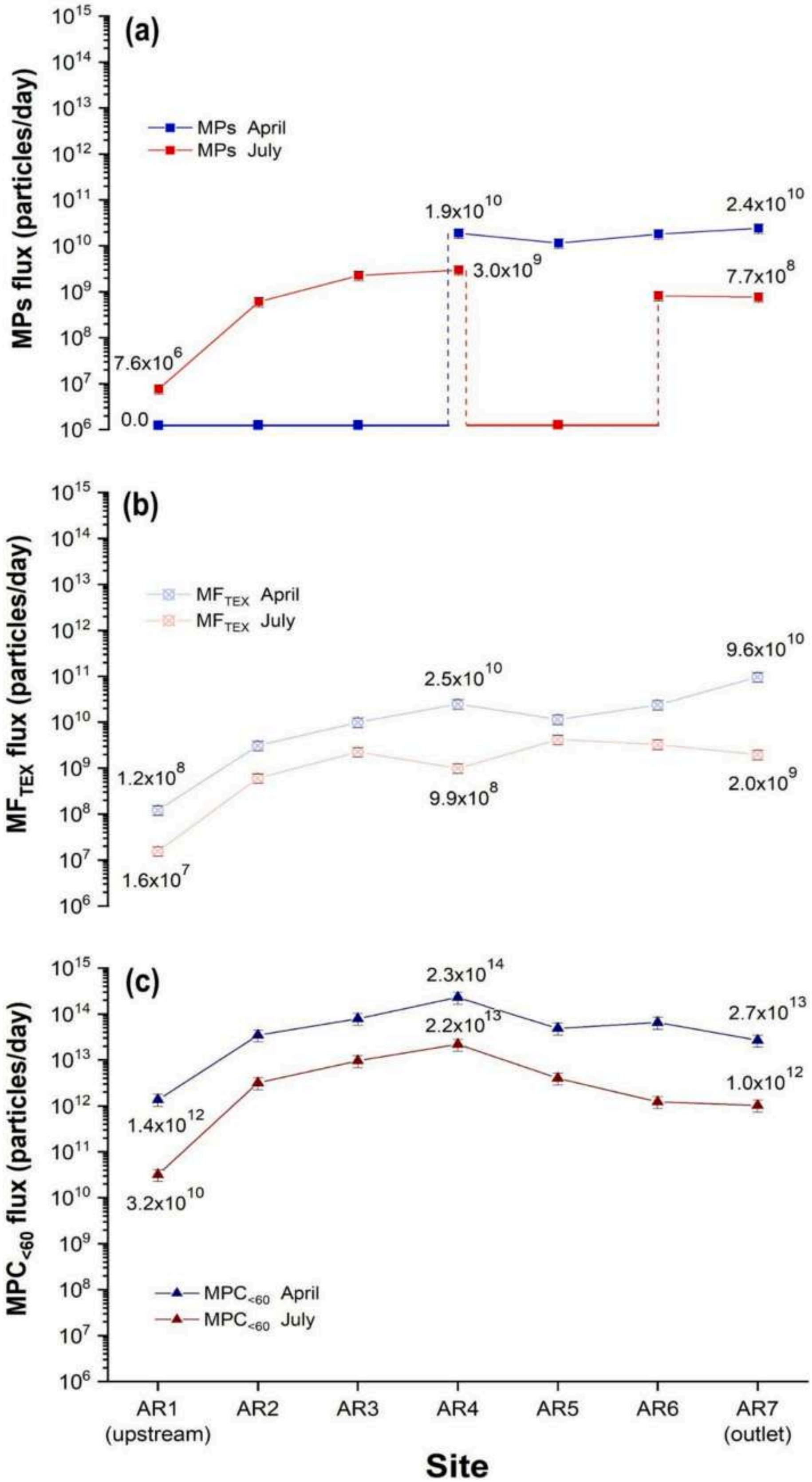

Fig. 6. Daily fluxes (particles/day) of (a) MPs, (b) MF_{TEX}, (c) $MPC_{<60}$ along the Arno River sampling points in April and July 2022 (semilog scale). At AR7 and AR4 fluxes were calculated considering MPC concentrations from the center of the river. Fluxes for left and right location are available in Table S2.

river mouth was observed also along the Ebro Delta (Simon-Sánchez et al., 2019) and in the surface waters of the Douro River estuary, Portugal (Rodrigues et al., 2019).

Water mixing seems to have a dilution effect on MPC in the Arno River, triggered by the intrusion of seawater at the river outlet, especially during the severe drought periods of the dry season (saline wedge) characterised by a stronger marine influence inland. In support of this hypothesis, lower MPs abundances ($7 \pm 13 \times 10^{-5}$ to $11 \pm 24 \times 10^{-5}$ particles/L) compared to those found in this study (3.9 ± 0.9 particles/L at AR7), were reported by Baini et al., 2018 along a transect located in front of the Arno River estuary (0.5 to 20 km to the Tuscan coast).

Seawater intrusion could also explain the seasonal differences in MPC ($MPC_{>60}$ and $MPC_{<60}$) concentrations along the river cross-section investigated at the outlet site (AR7).

In the absence of sea influence (April), river hydrodynamics show a major control on the $MPC_{>60}$ distribution across the Arno River cross-sections (Fig. 2b, c). The higher flow current velocity in the central part of the river, compared to the riverbanks, typical of river hydrodynamics (e.g., Gualtieri et al., 2017; Haberstroh et al., 2021), allows to hypothesize an easier MPC transport along the central river sectors compared to the shores.

At the inland site AR4, the influence of the sea is never recorded in the wet or dry seasons, and similarly at AR7, during the wet season (April) saline intrusion was not observed (E.C.: 656 μS/cm). Differently, the strong marine intrusion at AR7 in the dry season (E.C.: 9630 μS/cm) likely led to a homogenisation of the $MPC_{>60}$ abundance throughout the river section (centre/banks) (Fig. 2c). On the contrary, the spatial distribution of $MPC_{<60}$ concentration did not show any difference under any season.

According to the laboratory experiments carried out by Kowalski et al., 2016, Besseling et al., 2017, and Khatmullina and Isachenko, 2017, the terminal settling velocity of MPC with a micrometric size is lower than the one of millimetric size in riverine waters (Z. Yu et al., 2022). Therefore, we may assume that, under the Arno River hydrological conditions investigated in this study, the smallest particle fraction ($MPC_{<60}$) is more easily mobilised than the largest one ($MPC_{>60}$), and then not susceptible to riverbank effects.

The dominant presence (76 %) of $MPC_{>60}$ with fiber shape emerged in this study is in agreement with most of the research carried out in shallow riverine waters (Li et al., 2020; Lin et al., 2018; Napper et al., 2021). Their abundance could be partially explained by the lower settling velocity in aquatic environments, compared to other shapes (e.g., regular and irregular fragments), and by their ease of mobilizing, in agreement with Waldschläger and Schüttrumpf, 2019 and Khatmullina and Isachenko, 2017. In addition, the fibers dominance seems to be strictly dependent on the severe contribution from domestic and commercial sewage effluents associated with the laundering (washing and tumble drying) and the treatment (industrial wet processing) of manufactured textiles (e.g., garments). According to Hartline et al., 2016, Lambert and Wagner, 2018, and Rathinamoorthy and Raja Balasaraswathi, 2022, most microfibers are ascribed to daily laundry, which represents one of the main global sources of micro-litter. Indeed, all $MPC_{>60}$ fibers characterizing the Arno River waters were compositionally of natural or man-made cellulose (e.g., rayon) or synthetic polymers (e.g., PET) (Fig. 5a, b) typically involved in the production of textiles (Islam et al., 2020).

Specifically, textile microfibers (MF_{TEX} and PET) are particularly abundant at the city of Florence site (AR4), representing approximately 85 % of the $MPC_{>60}$ detected, and reaching concentrations up to 8.0 particles/L. This abundance is partly comparable to values (2.1 to 71.0 particles/L) found in the waterbodies draining the "China Textile City" (Shaoxing County, China), one of the largest textile manufacturing and trading centres in Asia (Deng et al., 2020), and higher than concentrations recorded at the downstream site AR5, where the Arno River receives the contribute from the textile district of Prato. Before being discharged into the rivers, industrial and municipal wastewater are processed by wastewater treatment plants (WWTPs) (Roex et al., 2013). Retention efficiency of these plants can be >90 %, according to the different treatment processes used at the various WWTPs (Talvitie et al., 2015; Waldschläger et al., 2020; Surana et al., 2024; Tserendorj et al., 2024) Despite that, a non-negligible amount of MPC is however released from WWTPs (Cristaldi et al., 2020). This is confirmed by Becucci et al., 2022, which recorded MPs mass transfer to the Arno River in the order of 35 kg/day (5 MPs/L) from the main WWTP serving the urban area of Florence (San Colombano; 600.000 p.e.). In the case of Florence, however, the microfiber abundance may be hardly ascribed to textile industrial activities since mass loads of MPC (both $MPC_{<60}$ and $MPC_{>60}$) at AR5 are lower or comparable to AR4 (Table S2 and Fig. 6). Most of the active businesses conducted in the town is rather associated to the tertiary sector (around 67 %), dominated by touristic activities (CCIAA Firenze, 2024). Florence is one of Italy's top destinations for tourists. It is regarded as the birthplace of the Renaissance, and since 1982 the historic centre was recognized as a UNESCO World Heritage Site for its "Outstanding Universal Value". Tourism in Florence peaked in 2019 with >4 million arrivals. Representing over 10 times the number of residents (Del Bianco and Montedoro, 2023) tourism makes up 11 % of the local economy (Liberatore et al., 2023). The city's accommodation capacity has grown exceptionally, with almost 16 million overnight stays (in 2019), and a city center average occupancy rate of 75 % (Liberatore et al., 2023), with the highest rate of Airbnb per 1000 inhabitants among the main destinations in the world (Higgins et al., 2023). The overflow of temporary visitors, so-called overtourism, while it certainly positively influences the local economy, may negatively impact the environment (de Oliveira et al., 2023) generating, among others, pressure on water resources to supply the increased demand, high use of the public sewage system, and a large volume of textile consumption at tourist facilities (e.g., hotels and B&B) by the daily use, disposal and cleaning of towels, sheets, tablecloths or napkins (Franco et al., 2023). Consequently, the observed increase of textile microfibers in Florence may be tentatively ascribed to the city's tourism industry, although to precisely ascertain this connection more focused research should be done in the next future.

Among MPs, PET $(C_{10}H_8O_4)_n$ is the most common synthetic polymer found in the Arno River; in fiber shape it may be associated with textile manufacturing, while as fragment it may derive from plastic bottles, which are considered among the major single-use plastic products marketed in Italy (Sharma et al., 2021). In particular, Italians are among the greatest consumers of bottled water in Europe (and globally), with 65 % of water in plastic bottles (Alessi et al., 2018) typically made of PET due to its excellent features such as resistance to impact, moisture, alcohols and solvents (Crawford and Quinn, 2016).

The other anthropogenic polymers found in the Arno River cover almost any use: PA $(C_6H_{11}NO)_n$, featuring high tensile strength and excellent abrasion resistance, is used mainly for food packaging films and textiles; ABS $(C_8H_8{\cdot}C_4H_6{\cdot}C_3H_3N)_n$, high in strength, hardness, impact resistance and rigidity, is used for pipe fittings, toys and auto parts; PMMA $C_5H_8O_2$, with excellent light transmissibility and good resistance to ultraviolet light and weathering, is used in car windows and smartphone screens; PAN $(C_3H_3N)_n$, heat resistant and able to form oriented fibers, is used for textile and water treatment; elastomers as Neoprene rubber (CR) $(C_4H_5Cl)_n$, featuring good mechanical strength and high-temperature resistance, are used mainly for automotive, medical, and packaging uses (Crawford and Quinn, 2016). Despite it's considered the most common MPs polymer in aquatic environments (Xun et al., 2024), no polypropylene (PP) $(C_3H_6)_n$ microparticles were found in this study. This apparent absence could be explained by the difficulty of discriminating aged PP and PE-PP blend particles during μ-FTIR analysis (Gicquel et al., 2024).

Because of their wide array of applications and their random distribution along the Arno River, no specific sources for the listed polymers can be identified.

4.2. Environmental assessment and water quality

Many studies in riverine environments all around the world have highlighted the presence of MPs (e.g. Lebreton et al., 2017; Schmidt et al., 2017; Gao et al., 2024) as major contaminants. Specifically, many research documented microfibers as the most common anthropogenic MPC in aquatic environments (wastewaters, e.g.; Grbić et al., 2020; rivers, e.g. Miller et al., 2017; estuaries, e.g. Naidoo et al., 2020; seas, e.g. Suaria et al., 2020; Acharya et al., 2021; Athey and Erdle, 2022). In fluvial waters it was also observed that microfibers represent the largest class of MPC found, such as in the Ebro River (Spain) (Simon-Sánchez et al., 2019), in the Hudson River (USA) (Miller et al., 2017) or in the East River and Long Island (USA) (Miller et al., 2024). Our study also found a non-trascurable quantity of fibers among MPC in the Arno River, among which MF_{TEX} represented around 70 % of all $MPC_{>60}$. These microfibres are not commonly considered in the quantification of MPs pollution with the assumption of their biodegradability in the environment, however, they are sufficiently persistent in aquatic systems to undergo long-range transport (Ladewig et al., 2015; Athey and Erdle, 2022) and they can cause adverse effects to organisms (Carney Almroth et al., 2021; Athey and Erdle, 2022). Although few studies quantified the presence of "natural" fibers in river environments, they indicate that they are a major presence in waters, such as in the East River and Long Island (USA), where 52 % of the fibers found were non-synthetic/anthropogenic (Miller et al., 2024), or in the Douro River (Portugal), where 63 % of the fibers were mostly natural (non-synthetic) (Prata et al., 2021). The present investigation further highlights the importance of including natural fibers, and specifically MF_{TEX}, in environmental studies. Although it was not possible to quantify the relative abundances of MF_{TEX} and the MPs in the $MPC_{<60}$ for analytical conditions (see 4.2), we can infer a high impact of these microfibres in the Arno River water, considering that this fraction ($MPC_{<60}$) represents almost 99 % of the total MPC contamination.

The environmental assessment of the Arno River waters and comparison with other studies is made difficult by the lack of standardized protocols for the sampling, extraction, and analysis of MPs in any environmental context. Another problematic parameter for reliable comparisons is the difference in the investigated MPC size range.

Dissimilarities in the dimensional range investigated can be mainly attributed to the increasing methodological complexity as the MPs size decreases: this causes a strong variability among authors, who commonly focus on the largest MPs fractions, diregarding the most abundant and impactful smallest fractions. In fact, as widely demonstrated here and in many other studies (Barrows et al., 2017; Han et al., 2020; Scircle et al., 2020; Prata et al., 2021; Carbery et al., 2022), the majority of MPs fall within the smaller size range, with an inversely proportional relationship between size and abundance, likely resulting from the persistent degradation processes acting on plastic debris. Furthermore, the uptake by lower trophic levels increases with smaller MPs size (Başaran Kankılıç et al., 2023; Lehtiniemi et al., 2018), with a consequent growing hazard for aquatic organisms. Studies carried out on shallow (Di Lorenzo et al., 2023) and groundwater (Sforzi et al., 2024) systems of the Florence alluvial plain highlighted how smaller MPs (<48 μm) can be easily found within the meiofaunal and groundwater taxa that populate these environments.

In light of all these observations, we therefore compared the Arno River water quality with studies investigating MPs size range similar to this work (60–5000 μm), allowing a more reliable assessment of the freshwater system examined. Next to the spring (AR1 site), the Arno showed MPs contaminations (up to 1.8 particles/L) higher than the ones reported in the literature for Indonesian spring river waters (Yanuar et al., 2024; 0.03–0.2 particles/L) and river courses crossing peri-urban and rural areas in Taiwan (Kunz et al., 2023; 0.01–0.02 particles/L). Similar abundances were reported along the countryside stretch of the Kosasthalaiyar River, India (Priyanka and Govindarajulu, 2023; 0.2–1.6 particles/L).

Considering all the fluvial course, the Arno River showed a water quality (up to 7.6 ± 1.8 particles/L) comparable to that of the Seine River (Dris et al., 2015: MPs range of 100–5000 μm; 3.0 particles/L; Treilles et al., 2022: MPs range of 80–5000 μm; 1.3–34.4 particles/L), whose large catchment surface (78,650 km^2) suffers the strong anthropic pressure of the Paris metropolitan area (12.5 million inhabitants in 2019).

Furthermore, the Arno River MPs pollution appears similar to other riverine systems worldwide, such as the very large Yangtze River (catchment of 1,800,000 km^2) in China (He et al., 2021) (MPs range of 48–5000 μm; 0.8–3.1 particles/L), and the smaller Cooks River (catchment of 100 km^2) in Australia (Hitchcock, 2020) (MPs range of 50–5000 μm; 0.4–17.4 particles/L), which drains the urban area of the city of Sydney (5 million inhabitants in 2017).

Overall, this work provided a first estimate of $MPC_{<60}$, MPs and MF_{TEX} (60–5000 μm in size) in the Arno River waters, highlighting challenges in analytical and methodological approaches in this kind of study.

4.3. MPC contribution to the Mediterranean Sea

The accumulation of micro-litters in oceans and seas is one of the most important global challenges that humanity is facing, with particular regard for MPs. The Mediterranean Sea is highly exposed to plastic pollution (Cincinelli et al., 2019; Sharma et al., 2021). Indeed, its semi-enclosed morphology and the rivers draining its surrounding densely populated area (~200 million people) promote a severe accumulation of MPC in the basin. However, studies on the presence of MPs in Mediterranean Sea tributary rivers are limited. In Table 1 we integrated the data of this study (Arno River) with MPs inputs from the three major catchments of the Mediterranean Sea (Nile, Rhone, Po) and other

Table 1
MPs fluxes into the Mediterranean Sea from different river catchments.

River	Country	Catchment area (km^2)	Yearly MPs flux into the Mediterranean Sea	MPs size range (μm)	Reference
Arno	Italy	8228	$2.2 \pm 0.5 \times 10^{12}$ particles/year 7.6 ± 1.8 t/y	60–5000	This study
Nile	Egypt	3,254,555	18.6×10^{10} particles/year * (6.15 t/y)[c]	55–5000	Shabaka et al., 2022
Rhone	France	95,500	5.92 t/y 22 t/y (flood events)	300/ 333–5000	Constant et al., 2020
Têt	France	1550	0.09 t/y	300/ 333–5000	
Po	Italy	71,000	145 t/y	300–5000	Munari et al., 2021
Ebro	Spain	86,100	2.14×10^9 particles/year	<50–5000	Simon-Sánchez et al., 2019
Pinios	Greece	9800	2.5×10^8 particles/year (wet season)[d] 1.4×10^7 particles/year (dry season)[d]	330–5000	Zeri et al., 2021
Kifissos	Greece	380[a]	5.5–5.0 $\times 10^7$ particles/year[d]	330–5000	
Göksu	Turkey	10,000[b]	1.07×10^{12} particles/year	26–5000	Özgüler et al., 2022

[a] According to Panagiotopoulos et al., 2010.
[b] According to Demirel et al., 2011.
[c] (Damietta branch + Rosetta branch).
[d] Estimated using reference data.

smaller watersheds, to improve knowledge of the MPs budgets from river systems to the marine basin. Mass discharges of MPs from the Arno River into the sea were calculated as plastic weight fluxes (t/y) for consistency with other studies (Constant et al., 2020; Munari et al., 2021; Shabaka et al., 2022) (S5, Supplementary material).

The daily discharges of MPs (fraction of $MPC_{>60}$) from the Arno River into the Mediterranean Sea varied from 11 billion MPs ($1.1 \pm 0.3 \times 10^{10}$ particles/day; 41.5 ± 9.7 kg/day) during the wet season to 0.5 billion MPs ($5.2 \pm 1.2 \times 10^{8}$ particles/day; 0.3 ± 0.1 kg/day) during the dry season. This seasonal variability highlights a likely key role of inland rainfalls in MPs mobilization. In detail, the great precipitations recorded in the river catchment during the wet season (1st-30th April 2022: 69 mm precipitation in Florence recorded at the station "Orto Botanico"; SIR, 2024) could trigger higher river flows (S4, Supplementary material, Table S2) and stronger runoff of the impervious urban surfaces, with the consequent increasing input and transport of MPs in the Arno River. Differently, the lower runoff of the dry season (1st–31st July 2022: 2 mm precipitation in Florence, "Orto Botanico"; SIR, 2024) may promote accumulation processes and, consequently, a comparatively minor MPs mobilization. Variations in MPs mobility strictly connected to the meteorological forcing (e.g., precipitations) on the catchment were also reported by other authors (Constant et al., 2020; Treilles et al., 2022), suggesting that rainy events favour MPs transportation along riverine systems up to the outlets, thus making contributions to the sea strongly variable under seasonal-dependent water regimes.

This effect seems to be confirmed by Baini et al., 2018, which found a higher plastic concentration (59,730 particles/km^2) in the Tyrrhenian waters adjacent to the Arno estuary (0.5 km off the Tuscan coast) than offshore (20 km off the coast) during the spring season, suggesting a marked terrestrial input from the river under flood conditions.

The definition of a representative budget of MPs from rivers to the sea is made more complex by the great spatial and temporal variability of MPs fluxes. The yearly average input of MPs to the sea was estimated considering the hydrological conditions investigated (wet and dry season), as representative of the whole year 2022 (S5, Supplementary material), to reduce uncertainties in this respect and to better estimate contributions from the Arno River into the Mediterranean Sea. An average discharge of 2.2 trillion MPs ($2.2 \pm 0.5 \times 10^{12}$ particles/year) was estimated, corresponding to 7.6 ± 1.8 tons of MPs arriving to the Mediterranean Sea each year.

Comparing the yearly MPs fluxes with the ones reported in the literature for the rivers flowing along the Mediterranean coasts (Table 1), the plastic microparticle's contribution (particles/year) from the Arno River is higher than most of the other tributary, such as the longest Nile, Egypt (Shabaka et al., 2022), Ebro, Spain (Simon-Sánchez et al., 2019), rivers of catchment size similar to the Arno, as Pinios, Greece (Zeri et al., 2021), and the shortest Kifissos River, Greece (Zeri et al., 2021), which suffers the anthropic impact of the metropolis of Athens (2.6 million inhabitants in 2011). The only exception is the Göksu River, Turkey (Özgüler et al., 2022), where MPs contribution was comparable to the Arno River.

By weight (t/y), the Arno River discharges a quantity of MPs higher than the small and less anthropised Têt River, France (Constant et al., 2020), and very similar to those reported for the more impacted Nile River (Shabaka et al., 2022) and Rhone River, France (Constant et al., 2020). Higher MPs mass load was highlighted for the Po River (Munari et al., 2021), the longest waterway in Italy, impacted by the anthropic pressure of many large cities and areas of intensive industrial and agricultural activities (15 million inhabitants in the catchment) (Fiore et al., 2022).

4.4. Mediterranean tributary rivers

As already noticed for abundances, differences in plastic micro-litter size range investigated among studies make comparisons of MPs contributions into the Mediterranean Sea problematic. Specifically, most of the comparative studies here reported, employed typical sampling approaches for off-shore research (Du et al., 2022), such as manta trawling, thus investigating larger MPs size fractions only (300/333–5000 μm), and consequently underestimating the comprehensive quality status of riverine waters and their impact in Mediterranean basin.

The same seasonal dependence on the meteorological forcing inland described for MPs, was observed by daily discharges of MF_{TEX} and $MPC_{<60}$ (Table S3). Contributions of MF_{TEX} into the Mediterranean Sea was of $4.7 \pm 1.1 \times 10^{10}$ particles/day (5.2 ± 1.2 kg/day) in April and $2.4 \pm 0.6 \times 10^{9}$ particles/day (0.3 ± 0.1 kg/day) in July, and $MPC_{<60}$ discharge was of $2.4 \pm 0.7 \times 10^{13}$ particles/day (108 ± 25 kg/day) in April and $1.2 \pm 0.3 \times 10^{12}$ particles/day (5.3 ± 1.3 kg/day) in July. Also, the yearly average input of MF_{TEX} and $MPC_{<60}$ to the sea (estimated as MPs S5, Supplementary material), showed values respectively of $1.2 \pm 0.3 \times 10^{12}$ particles/year (1.0 ± 0.2 t/y) and $4.6 \pm 1.3 \times 10^{15}$ particles/year (21 ± 5 t/y). To the best of our knowledge, these estimations of the Arno River are the first available loads of MF_{TEX} for a river discharging to the Mediterranean Sea.

If we include these two fractions to the Arno River MPs budget, an important mass of 29.4 ± 6.9 tons of micro-litter particles (MPC_{TOT}, 5–5000 μm), is annually discharged in the Mediterranean Sea. Around 71 % of MPC_{TOT} yearly tonnage is associated with the fraction of $MPC_{<60}$, which is confirmed as the dominant and most environmentally impactful MPC fraction in the Arno River waters, while $MPC_{>60}$ fractions (MPs and MF_{TEX}) represent 26 % and 3 % of the annual mass load, respectively. Given the analytical difficulties in the discrimination between MPs and MF_{TEX} in the fraction smaller than 60 μm, the respective contribution in the Mediterranean Sea for these two different micro-litter particles has not been estimated, highlighting a topic which needs to be addressed in the future.

Finally, even if beyond the scope of the paper, we briefly discuss possible measures to reduce contamination of the Arno River. A typical approach by many governments and policymakers is to limit, or even ban, the production and/or the use of plastic particles such as shopping bags and water bottles (e.g., Laskar and Kumar, 2019). It is however impossible to ban or limit many sources of MPs and microfibers such as industrial plastic supplies, industrial textiles, car tires or clothing. It seems therefore necessary to improve the filtering systems to remove MPC from wastewaters at the urban or household scale. However, elimination of the smallest microfibers or microfragments will remain a challenging task. Even applying cutting-edge technologies, a fraction of MPC will reach the aquatic ecosystem (e.g. Arias et al., 2022; Athey and Erdle, 2022), impacting riverine and sea environment. In any case, implementation of more efficient filtering systems at the point sources would achieve at least a mitigation of the impact.

5. Conclusions

For the first time, microplastics (MPs) and natural-based textile fibers (MF_{TEX}) were investigated in the waters of the Arno River, the main waterway of Tuscany (Central Italy). A specific methodical approach (sampling, processing, and analysis) was developed to allow the detection of microparticles (MPC) covering a wide size range (5–5000 μm, MPC_{TOT}).

Results show that the Arno is affected by MPC_{TOT} (MPs + MF_{TEX}) contamination all along the river (up to 56,011 ± 16,411 particles/L), mostly represented by particles smaller than 60 μm ($MPC_{<60}$), which account for >99 % of the total. Morphological and chemical characterization of MPC larger than 60 μm ($MPC_{>60}$) highlighted a predominance (85 %) of natural-based textile and synthetic polymer microfibers (essentially PET), strictly associated with textile manufacture. For this reason, a strong contribution from domestic and industrial laundry effluents throughout the river was hypothesized. In particular, the metropolitan area of the city of Florence was identified as a MPC_{TOT} hotspot. Here, the recorded deterioration of the Arno River water quality might be related to the intense urbanization, possibly with a significant contribution of the high tourist activity affecting the city.

Despite the lack of uniform methodology protocols, which makes difficult to make comparisons with other published studies, the Arno River is a freshwater system characterised by a significant MPC_{TOT} contamination, with MPs concentrations in water (up to 7.6 ± 1.8 particles/L) comparable to polluted fluvial systems worldwide (e.g., Seine River, Yangtze River) and up to 9.8 ± 2.3 of MF_{TEX}. Consequently, the yearly MPC_{TOT} discharge at the river outlet ($4.6 \pm 1.3 \times 10^{15}$ particles/year; 30 ± 7 t/y) suggests that the Arno River can negatively impact the Mediterranean Sea and its marine ecosystems. Mobilization of micro-litter and discharges to the Sea are controlled by the meteorological forcing inland. Rainfall events in the Arno's catchment area during the spring season likely trigger run-off on impervious urban surfaces and favour micro-litter transport from inland to the sea ($2.4 \pm 0.7 \times 10^{13}$ particles/day; 155 ± 36 kg/day), while the water scarcity recorded during the summer drought period favour sedimentation and accumulation of MPC_{TOT}, with a consequent reduction in micro-litter contribution to the sea ($1.2 \pm 0.3 \times 10^{12}$ particles/day; 6 ± 1 kg/day). The WWTPs installed in the catchment seems insufficient to substantially reduce MPC_{TOT} pollution in the Arno River waters.

This study suggests that to correctly assess the impact of micro-litters in riverine and marine ecosystems, MPs and MF_{TEX} should be explicitly characterised in the widest size range. The urgent need to adopt universal criteria to facilitate the comparison among studies is also highlighted.

CRediT authorship contribution statement

Valentina Rimondi: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Data curation, Conceptualization. **Guia Morelli:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization. **Alessia Nannoni:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Alessandra Cincinelli:** Writing – original draft, Validation, Methodology, Formal analysis. **Tania Martellini:** Validation, Methodology, Formal analysis. **David Chelazzi:** Writing – original draft, Formal analysis, Data curation. **Marco Laurati:** Writing – original draft, Validation, Formal analysis. **Laura Sforzi:** Writing – original draft, Formal analysis, Data curation. **Francesco Ciani:** Investigation, Data curation. **Pierfranco Lattanzi:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Pilario Costagliola:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation, Conceptualization.

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.

Acknowledgements

A.C. and L.S. acknowledge co-funding from Next Generation EU, in the context of the National Recovery and Resilience Plan, M4C2 Investment 1.3, PE_00000005, "RETURN", CUP B83C22004820002. This resource was co-financed by the Next Generation EU. The views and opinions expressed are only those of the authors and do not necessarily reflect those of the European Union or the European Commission. Neither the European Union nor the European Commission can be held responsible for them. The final version benefited immensely from the perceptive criticism of two anonymous reviewers. They share any credit and no blame for this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.177113.

Data availability

Data will be made available on request.

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