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Comparison of plastic pollution between waters and sediments in four Po River tributaries (Northern Italy)

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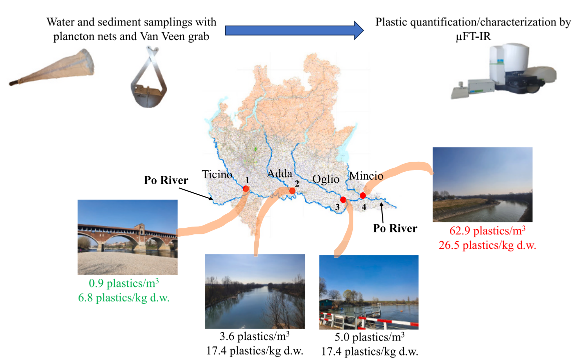
HIGHLIGHTS

- Plastic monitoring in waters and sediments of 4 Italian rivers was performed.
- Plastic contamination in sediments was 4 times higher than in waters.
- Ticino River showed the lowest plastic contamination and Mincio River the highest.
- Plastic pollution of selected rivers is comparable to other European water courses.

GRAPHICAL ABSTRACT



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ABSTRACT

The monitoring of plastic contamination in freshwaters is still pioneering in comparison with marine environments, and few studies analyzed the distribution of these pollutants in both aqueous and bottom compartments of continental waters. Therefore, the aim of this study was the comparison of plastic pollution in both waters and sediments of four Po River tributaries (Ticino, Adda, Oglio and Mincio Rivers), which outflow from the main Italian sub-alpine Lakes, in order to establish the strengths and weaknesses of both matrices. The main results pointed out a heterogeneous plastic contamination, with the lowest values in Ticino (0.9 ± 0.5 plastics/m^3 in waters and 6.8 ± 4.5 plastics/kg dry weight - d.w. - in sediments) and the highest in Mincio (62.9 ± 53.9 plastics/m^3 in waters and 26.5 ± 13.3 plastics/kg d.w in sediments), highlighting a plastic amount in sediments four times higher than waters. Plastic pollution, mainly due to microplastics, was associated principally to a domestic input in both waters and sediments of Ticino and Adda Rivers, as well as in sediments of Oglio, while an industrial pollution was found in waters and sediments of Mincio and Oglio waters. Our data clearly highlighted as the monitoring of both matrices provide complementary information for a holistic risk assessment of these emerging contaminants in freshwaters: the aqueous matrix provides an instantaneous picture of contamination, while sediments the history of pollution.

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1. Introduction

Plastics are synthetic materials widely used in our daily life due to their particular chemical/physical proprieties, associated to the low costs of production (Andrady and Neal, 2009; Soares et al., 2021; Pandey et al., 2023). For these reasons, the plastic demand follows a positive trend worldwide, resulting in an increase of plastic production that reached 391 million tons (Mt) in 2021 (Plastics Europe, 2022). Despite this high production, the Organisation for Economic Cooperation and Development (OECD, 2022) highlighted that only 9 % of produced plastics is recycled, 19 % is burned and turned into fuel and other products, 50 % is disposed in landfills, while the remaining 22 % escapes from the waste management and is dispersed in the environment. Even if Oceans represent the final compartment where plastics are accumulated, 80 % of this pollution come from continental areas (Andrady, 2011). More specifically, 88–95 % of the total plastic flux to the seas derives from only ten rivers, eight of which in Asia and two in Africa, where the Nile transports about 3.29 Mt of plastics into the Mediterranean Sea every year (Schmidt et al., 2017). Moreover, the Asian rivers Yangtze and Indus are the main contaminated water courses worldwide with an annual plastic input of 16.88 and 4.81 Mt into Yellow and Arabian Seas, respectively (Schmidt et al., 2017). European rivers also contribute to the inflow of plastic particles to the marine environment, since it was estimated that Rhine River releases from 16.0 to 58.8 tons of plastics *per* year in the North Sea (van Emmerik et al., 2022a), while Po River, the main Italian water course, contributes annually about 145 tons of plastics to the Mediterranean Sea (Munari et al., 2021).

Although the main evidence of plastic pollution is focused to the water matrix, also the river sediments are potentially heavily impacted by plastics, due to the capability of these contaminants to settle down on the river bottom (Daily and Hoffman, 2020). Indeed, whereas low-density polymers, such as polyethylene (PE), polypropylene (PP) and polystyrene (PS; Crawford and Quinn, 2017), can float on water surface negatively affecting both nekton and plankton components (De Marco et al., 2022; Kokali et al., 2022), high-density polymers, such as polyvinyl chloride (PVC), are more prone to settle on the bottom impacting the benthic organisms. This aspect was recently reported by Prata et al. (2023), who found the damage of the gut epithelium by high-density polymers in *Chironomus* sp. Floating plastics can also become a growth substrate for various microorganisms, through the biofouling, inducing their settlement and increasing the sediment contamination (Lobelle and Cunliffe, 2011; Woodall et al., 2014). In addition, the presence of plastics could change the sediment properties, leading to alterations in organism behavior, as well as modulating the toxicity of other pollutants (Prata et al., 2023). In this context, some Asian water courses, such as Wen-Rui Tang and West Rivers (China), showed a dramatic sediment contamination of 32,947 plastics/kg dry weight (d.w.; Wang et al., 2018) and 10,240 plastics/kg d.w. (Huang et al., 2021), respectively. Moving to European Countries, the most polluted river sediments seem to be those observed in Arno River (Italy) in which a plastic level up to 5680 plastics/kg d.w. was found (Ghinassi et al., 2023), Ebro River (Spain) with a plastic concentration up to 2052 plastics/kg d.w. (Simon-Sanchez et al., 2019) and in German Rhine River (up to 3763 plastics/kg d.w.; Klein et al., 2015).

Although there are now several papers that report monitoring data of plastics both in waters and in river sediments, to our knowledge, none addresses a broad critical discussion of comparison regarding the advantages and drawbacks in the sampling of these two environmental matrices. Based on this knowledge gap in considering the fate of plastics in a riverine environment, the rationale of this study was the comparison of plastic distribution between waters and sediments sampled contemporarily, examining the best cost-benefit compromise on what environmental matrix should be sampled (waters - floating plastics, sediments - settleable plastics) for a correct assessment of plastic pollution in the context of a future and desirable routinary monitoring and risk assessment. To achieve this objective, we decided to quantify and characterize the plastics in waters and sediments of four different rivers in order to have a broad picture of the differences in contamination in these two environmental matrices. In detail, we sampled Ticino, Adda, Oglio and Mincio Rivers (Northern Italy) which are both among the main tributaries of Po River, the longest Italian river, and the outflows of the four largest and deepest subalpine Italian lakes, in which a plastic contamination from 11,000 plastics/km^2 in Lake Iseo up to 100,000 plastics/km^2 in Lake Maggiore was observed (Binelli et al., 2020).

2. Materials and methods

2.1. Study area

Ticino, Adda, Oglio and Mincio Rivers cross the Po Valley, one of the main industrialized and urbanized areas in Europe. To estimate the potential contribution of plastic inflow of each selected water course to Po River, we performed the samplings of both floating and settleable plastics near the confluence with the main Italian river (Fig. 1).

The Ticino spring is located in Switzerland, and the Italian tract is represented by the outflow of Lake Maggiore. This part of Ticino River reaches Po after 110 km, receiving the effluents of 156 Wastewater Treatment Plants (WWTPs), also considering those that discharge in the 11 Ticino tributaries (information kindly provided by Acqua Novara VCO s.p.a., Regione Piemonte - Direzione Ambiente, Energia e Territorio and ARPA Lombardia). The sampling site for this river was located under the Ponte Coperto (45.181389, 9.153611) in Pavia municipality (Fig. 1).

Adda River, with its 313 km, is the fourth longest Italian river after Po, Adige and Tevere, and receives 342 WWTP effluents (directly and from its 14 tributaries; ARPA Lombardia). The sampling site was located under the bridge of Provincial Road 47 (45.155259, 9.853735), near Crotta d'Adda municipality (Fig. 1).

Oglio River is the second longest tributary (280 km) of Po River after Adda. It crosses four big provinces in Lombardy, such as Brescia, Bergamo, Cremona and Mantova, and receives water from 308 WWTPs (directly and from its 28 tributaries; ARPA Lombardia). Samples were collected at Ponte di Barche (45.040801, 10.650687; Fig. 1).

Lastly, Mincio River is the shortest of the analyzed rivers (75 km) and receives 49 WWTP effluents (directly and from its 18 tributaries; ARPA Lombardia). The sampling site was located under the bridge of Governolo (45.084584, 10.953248; Fig. 1).

2.2. Samplings

Sediments and floating plastics were sampled from 1st June to 8th June 2022, collecting the matrices from the same water course in the same day. In this period, we registered constant weather conditions, characterized by lack of precipitations.

Sediments were collected by a Van Veen grab (sampling area of 200 cm^2; Scubla, Italy), dipped into the water by the last bridge before the confluence, and performing the sampling in triplicate. Simultaneously, to collect floating plastics, the river waters were filtered by three plankton nets (Scubla, Italy) with 100 μm mesh placed in the center of the water flow for 15 min (Binelli et al., 2022; Magni et al., 2021, 2022b). One net was equipped with a flowmeter (General Oceanics, Inc., Model 2030R) to calculate the volume of filtered water. After each sampling, both grab and nets were washed with 500 mL of distilled water and the collected material was then placed in 500 mL glass bottles with a metal cap. All samples were stored at 4 °C before the analysis.

2.3. Sediment characterization

Since sediment grain size could influence plastic retention, we analyzed it with water and organic matter (OM) contents, using 200 g sediment wet weight (w.w.). These were first dried at a temperature of 100 °C for 24 h to evaluate the water content and the relative d.w. After drying, 10 g sediment sample were muffled in ceramic crucibles at 550 °C for 8 h to remove all organic particles. Total OM was determined by loss between sediment d.w. (100 °C, 24 h) and after combustion residue weight (550 °C, 8 h; Fabiano et al., 1995).

Grain size analyses were carried out on river sediments through the use of cascade sieves with decreasing mesh size: 8, 1, 0.6, 0.25, 0.125, 0.063 and 0.030 mm and of a mechanical sieve shaker operating at 1.75 Hz and 15 min sieving time. Only dried samples were analyzed, classified based on Wentworth (1922) classification, and each sieve content was weighed to evaluate the percent abundance of river sediment *per* size class. All samples were weighed on a digital scale (PCE Instruments BSK 1100) with an accuracy of 0.01 g.

The chosen mesh sizes characterized four main grain size types: fine gravel (8 ÷ 2 mm), coarse to fine sand (2 ÷ 0.063 mm), medium to fine silt (0.063 ÷ 0.004 mm) and clay (<0.004 mm).

2.4. Sample processing and plastic extraction

As reported by Magni and Sbarberi (2022) in a preliminary study on the monitoring of plastics in the sediments of Lambro River (Northern Italy), it is necessary to perform the plastic extraction from sediments by using a higher density solution than sodium chloride (NaCl), normally used to process water samples, which contain low-density plastics (Magni et al., 2019, 2021, 2022b). For this reason, as suggested by Mattson et al. (2022), we used a hypersaline solution of zinc chloride ($ZnCl_2$; density of 1.6 g/cm^3) in the processing of sediments, and NaCl hypersaline solution (density of 1.2 g/cm^3) for the separation of plastics from the aqueous matrix of the four rivers. Indeed, NaCl is cheaper and harmless than $ZnCl_2$, which is corrosive in water, and the obtained density of NaCl solution is enough for the extraction of floating polymers (Constant et al., 2021).

In detail, 500 g w.w for each replicate of sediments were placed in 1 L $ZnCl_2$ hypersaline solution, stirred for 5 min using a magnetic stirrer, and decanted overnight to separate the plastics from the matrix due to a different density gradient. Prior to use, the hypersaline solution was filtered using a vacuum pump on glass fiber filters with 1.2 μm mesh (Whatman GF/C 47 mm) to eliminate the possible interfering material and also the potential plastics present. Lastly, 500 g w.w. sediment from each river and each replicate was dried at 95 °C for three days to evaluate the d.w.

Regarding the plastics in the water samples, the contents of each bottle were passed through two overlapped sieves, the upper one of 5 mm and the lower one with 63 μm mesh size. The filtered materials were rinsed and collected in glass bottles using 1 L of NaCl hypersaline solution, previously filtered as performed for $ZnCl_2$ solution, to separate the plastics from organic matter (Magni et al., 2021). The coarse materials collected on the sieves, as leaves, small size twigs and pebbles, were washed with another aliquot of NaCl hypersaline solution to prevent the loss of any plastics adhering to their surface, and then removed manually with metal tweezers.

After the overnight separation, the supernatant of both water and sediment samples was filtered using a vacuum pump on nitrate cellulose membrane filters with 8 μm mesh size (Sartorius™ 50 mm), and digested with hydrogen peroxide (H_2O_2, 15 % *v/v*) to remove all organic matter. The filters were then dried in Petri dishes under a laminar flow hood. To avoid plastic contamination of the samples, filters were kept covered when possible and lab cotton coats were worn during the sample treatments. To control the potential laboratory contamination by plastic particles, 2 filters for waters (one for sample processing and one for sample filtration), and one filter for sediments (same filters for weighing and filtration) were processed as blank for each replicate (Magni et al., 2019), for a total of 36 blank filters (24 for waters and 12 for sediments). Samples were corrected to the blank, when blank particles showed the same characteristics of sample plastics (same shape, colour and polymer).

2.5. Plastic quantification and characterization

Since the obtained filters from water and sediments were rich in interfering materials, the visual sorting by a stereomicroscope was

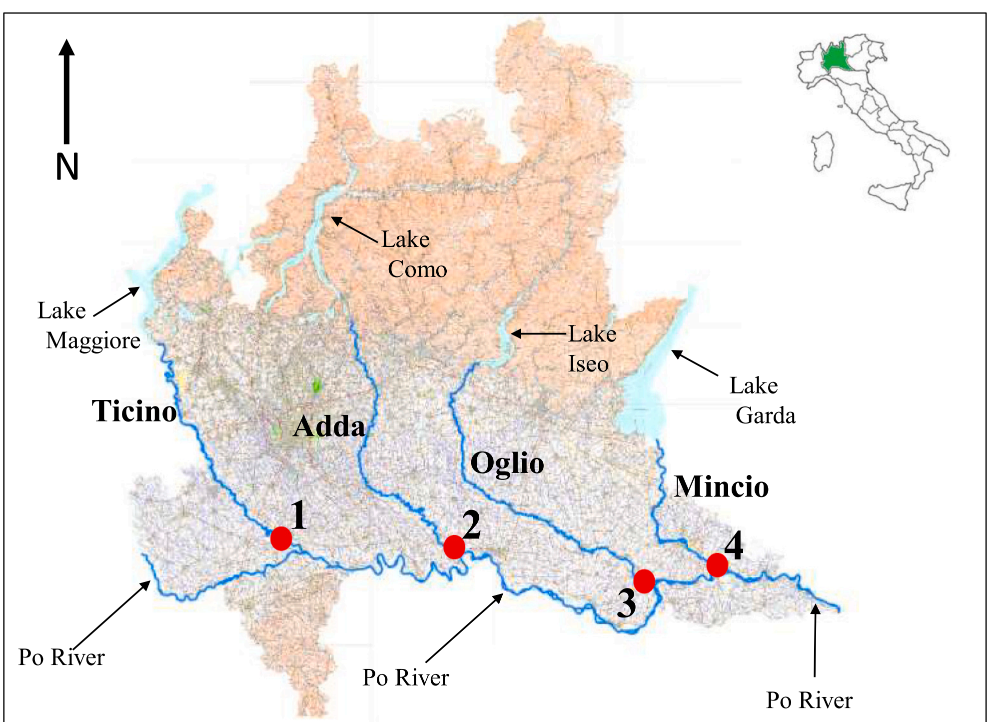

Fig. 1. Sampling stations in the Lombardy Region (red dots; Northern Italy) in Ticino (1), Adda (2), Oglio (3) and Mincio (4) Rivers. The selected sites are close to the confluence with the Po River (modified by www.geoportale.regione.lombardia.it).

necessary to move the suspected plastic particles on a clean filter.

The Fourier Transform Infrared Microscope System (μFT-IR; Spotlight 200i equipped with Spectrum Two, PerkinElmer) was used to quantify and characterize plastic polymers in attenuated total reflectance (ATR) with 32 scans in the wavelength range between 600 and 4000 cm^{-1}. Spectra were analyzed with Spectrum 10 software and compared with libraries of standards (PerkinElmer). Through visual sorting, we selected a total of 981 particles both in water and sediments of the four tributaries and then analyzed one by one by μFT-IR for the subsequent characterization.

Similarity of measured sample and reference spectrum was accepted only after visual examination of spectrum peaks and considering a matching score $\geq$ 0.70 (Magni et al., 2019). Plastic particles were classified according to their shape, as lines (same thickness in all length with sharp ends; Magni et al., 2019), fibers (ribbon-like shape with frayed ends; Almroth et al., 2018; Dris et al., 2018), films, fragments and pellets, as well as to their size, through ImageJ software. According to Hartmann et al. (2019) classification we categorized particles as: macroplastics $\geq$ 1 cm, 1 mm $<$ mesoplastics $<$ 10 mm, 1 μm $<$ microplastics $<$ 1 mm. Plastic colour was also recorded. The amount of synthetic particles was expressed as number of plastics *per* kilogram of sediment d.w. (plastics/kg d.w.), as well as plastics *per* cubic meter of water (plastics/m^3). In addition, to allow direct comparison of the amount of plastics in sediments and waters, we expressed the floating plastics also as plastics *per* kg of water (plastics/kg = plastics/L; 1 m^3 of water ≈1000 kg).

2.6. Statistical approach

The number of plastics in each river was compared using the one-way analysis of variance (ANOVA). In addition, to observe the potential covariation between the characterized parameters of sediments (grain size, water and OM contents), plastics in the aqueous matrix and in sediments, we performed the Pearson's correlation. The STATISTICA 7.0 software package was used.

3. Results

3.1. Sediment characterization

In Table S1 are reported the sediment grain sizes from the four sampled rivers. Sediments from Ticino River showed different texture compared to the similar composition observed in Oglio, Adda and Mincio Rivers. Indeed, Ticino River sediments showed a size higher than 8 mm (gravel; 49 %) and 1 mm (fine gravel; 28 %), while the other water bodies had a finer particle distribution in the range >0.25 mm (sand) and >1 mm. However, Mincio sediments showed the highest silt percentage (7 %) than the other water courses (range 0–0.2 %). Water content analyses reflected grain size results: Ticino River sediments, with higher gravel percentage, had the lowest water content (7 %), while the other 3 rivers showed values higher than 17 %. On the contrary, Mincio River sediments had the highest OM content (about 2 %) compared to the other rivers (Table S1). Despite these differences in terms of grain size, no significant covariation was observed between the measured parameters of sediments and the plastic retention in the river bottom. Moreover, no covariation was obtained between plastics in sediments and the related content in waters (p value in the range 0.149–0.903 for all considered parameters; Table S2).

3.2. Check of laboratory contamination by plastics

Blank filters analyses showed a negligible contamination by plastic items in our laboratories. Indeed, in the 24 blank filters used for water samples, we observed only 4 plastic items (3 fibers of polyester - PEST - and 1 fragment of PVC). Moving to sediments, in the 12 blank filters, 9 plastic particles were found (3 fibers of polyacrylate - PAK - 2 fibers of PEST, 1 fragment of PVC, 1 fragment of polystyrene - PS - and 2 fragment of polypropylene - PP). Considering the physical characteristics of the plastic particles detected in the blanks, as shape, colour and polymer, we removed only 1 transparent PEST fiber from the final count of plastics in water of Adda River, while 1 black PAK fiber and 1 transparent PEST fiber were eliminated from the plastic count in sediments of Ticino River.

3.3. Plastic monitoring in water and sediments from Po River tributaries

The whole dataset of physical and polymeric plastic characteristics identified by μFT-IR is reported in Table S3.

From a qualitative point of view, it should be emphasized that of the 981 particles subjected to instrumental analysis, only 36 % were recognized as synthetic polymers, 55 % were natural materials, while only on 9 % particles remained unidentified due to interfering substances deposited on their surface not digested by the H_2O_2, as also reported by Scherer et al. (2020).

3.3.1. Ticino River

We analyzed a total of 75 particles in the three water replicates from this tributary, identifying 15 plastic items, which represented only 20 % of the total analyzed particles (Table S3). The other 56 particles (75 %) had a natural origin, mainly cellulose, while 4 out of 75 items were not identified (5 %). Considering that the filtered water volume from Ticino River was 5.83 m^3, the mean plastic concentration was 0.9 ± 0.5 plastics/m^3 (Table 1 and Fig. 2A). Moving to sediment plastics, we analyzed a total of 152 particles, of which only 9 were plastics (6 %; Table S3) resulting in a mean concentration of 6.8 ± 4.5 plastics/kg sediments d.w. (Table 2 and Fig. 2B). We observed that even 138 items (91 %) had a natural origin and 5 were unknown (3 %). To directly compare data obtained for plastic contamination in the two environmental matrices, we also transformed the conventional unit of measurement in water (plastics/m^3) into the number of plastics *per* kg of water, as previously explained. Thus, we obtained a concentration of 0.0009 plastics/kg of water (Table 1). This value is not statistically significant different to the one calculated for sediments (6.8 ± 4.5 plastics/kg sediments d.w.; Fig. 2C).

Characterization of detected plastics is shown in Fig. 3 as size, highlighting microplastics were the main particles found, with similar percentages in waters (80 %) and sediments (78 %). A small different size distribution was observed between the two matrices, with the highest size value observed in the sediments (Fig. 4). Regarding shape, fibers were the main detected plastics in both matrices (60 % in waters and 78 % in sediments), while fragments were the second most detected shape in waters (33 %) followed by pellets (7 %) that were not found in sediments, while lines and fragments had the same percentage (11 %) in this matrix (Fig. 5). In this context, we integrated the shape with the polymer composition as reported in Fig. 6. Focusing only to fibers, the dominant shape of detected plastic items, waters seemed to be more heterogeneous in polymer composition than sediments because, notwithstanding a higher PEST fiber percentage was found both in waters (44 %) and sediments (71 %), water fibers included PP (22 %), PAK (22 %) and PVC (11 %), while in sediments the same percentage of fibers only in PP and Kevlar (14 %) were found (Fig. 6).

Lastly, the colours of plastics are also considered for their potential importance in prey/predator relationship: transparent and blue were the main detected particles in water (33 % and 27 %, respectively), while black was the main colour in sediments (23 %), followed by blue and orange (22 %) with the same percentage.

3.3.2. Adda River

As observed for Ticino, in the water of Adda River we detected a total of 75 particles in the three replicates, with a ratio of 19 plastics (25 % of the total; Table S3). The other 46 particles presented a natural origin (61 %), and 10 were unknown particles (13 %). In Adda sediments we

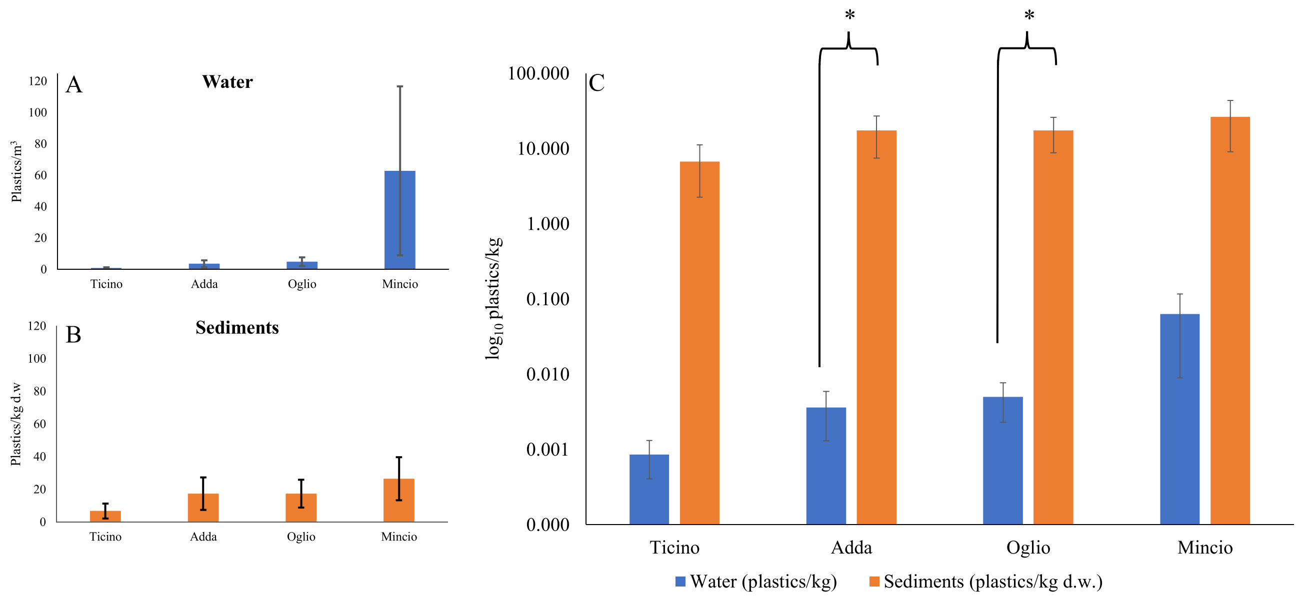

Fig. 2. (A) Number of plastics/m^3 (mean ± standard deviation SD) detected in river freshwater. (B) Number of plastics/kg d.w. (mean ± SD) detected in river sediments. (C) Comparison of the number of plastics/kg (expressed as $\log_{10}$; mean ± SD) in both waters and sediments of the selected rivers. Asterisks indicate significant differences (one-way ANOVA, $p < 0.05$) in terms of plastic content between waters and sediments of the same river (within group). No significant differences ($p > 0.05$) were observed between rivers regarding plastic content in both waters and sediments (between groups; A, B).

Table 1
Water volumes filtered and plastics detected in waters of selected rivers (mean ± SD). [a]Values obtained by flowmeter during the 15 min of sampling. [b]Values of sampling day at the confluence with Po River ([c]Pavia - Ticino, [d]Pizzighettone - Adda and [e]Marcaria - Oglio; [f]data for Mincio was not available due to the absence of flow sensors at the Po confluence). Information kindly provided by ARPA Lombardia.

River	Water volume filtered[a] (m^3)	Number of plastics identified (mean ± SD)	Plastics/m^3	Plastics/kg of water	Mean flow rate m^3/s[b]	Plastics/day into Po River
Ticino	5.83	5.0 ± 2.7	0.9 ± 0.5	0.0009	62.65[c]	4,655,146
Adda	1.75	6.3 ± 4.0	3.6 ± 2.3	0.0036	64.06[d]	19,980,570
Oglio	0.94	4.7 ± 2.6	5.0 ± 2.7	0.0050	30.50[e]	13,149,648
Mincio	1.17	73.7 ± 63.1	62.9 ± 53.9	0.0629	–[f]	–

Table 2
Quantity of analyzed sediments of the selected rivers and plastics detected (mean ± SD).

River	Quantity of analyzed sediment (g w.w.)	Number of plastics identified (mean ± SD)	Quantity of dry sediment (g d.w.)	Plastics/kg d.w.
Ticino	500	3.0 ± 2.0	444.7	6.8 ± 4.5
Adda	500	7.3 ± 4.2	422.0	17.4 ± 9.9
Oglio	500	7.0 ± 3.5	402.7	17.4 ± 8.6
Mincio	500	10.3 ± 6.8	390.0	26.5 ± 13.3

analyzed 88 particles, of which 22 plastics (25 %; Table S3), 60 with a natural origin (68 %) and 6 unknown (7 %). Therefore, the concentration of plastics ranged from 3.6 ± 2.3 plastics/m^3 (Table 1 and Fig. 2A), considering the filtered volume of 1.75 m^3 (0.00361 plastics/kg; Table 1), to 17.4 ± 9.9 plastics/kg sediments d.w. (Table 2 and Fig. 2B). In this context, we observed a significant increase of plastics ($F_{1,4} = 9.303821$; $p < 0.05$) in the sediments of Adda River compared to water (Fig. 2C).

Plastic characterization, in both waters and sediments showed mainly microplastics, with percentages of 84 % and 64 %, respectively (Fig. 3), as well as a similar size distribution (Fig. 4). Fibers were the main detected plastics, with 58 % in waters, followed by fragments (42 %), and 62 % in sediments, followed by lines (24 %) and fragments (14 %; Fig. 5). Considering the shape-polymer interaction, PEST was the main fiber polymer in both matrices, 100 % in sediments and 55 % in waters. Water matrix was also characterized by high PAK fiber percentages (18 %) and fragments of both PP (62 %) and PE (37 %), while sediments showed high Kevlar lines (80 %; Fig. 6).

The main detected colours in waters were black (27 %), followed by blue (26 %) and red (21 %), in the same way, in sediments black was the main colour (41 %), followed by transparent (27 %) and orange (14 %).

3.3.3. *Oglio River*

In this water course we detected a total of 67 particles in three water replicates, with a ratio of 14 plastics (21 %; Table S3), 51 particles with natural origin (76 %), and 2 unknown particles (3 %). In Oglio sediments we analyzed 111 particles, of which 21 plastics (19 %; Table S3), 83 with natural origin (75 %) and 7 unknown (6 %). Therefore, plastic concentration ranged from 5.0 ± 2.7 plastics/m^3 (Table 1 and Fig. 2A), considering the filtered volume of 0.94 m^3 (0.00499 plastics/kg; Table 1), to 17.4 ± 8.6 plastics/kg sediments d.w. (Table 2 and Fig. 2B). As observed for Adda, a significant increase of plastics ($F_{1,4} = 12.24297$; $p < 0.05$) in Oglio River sediments was obtained compared to waters (Fig. 2C).

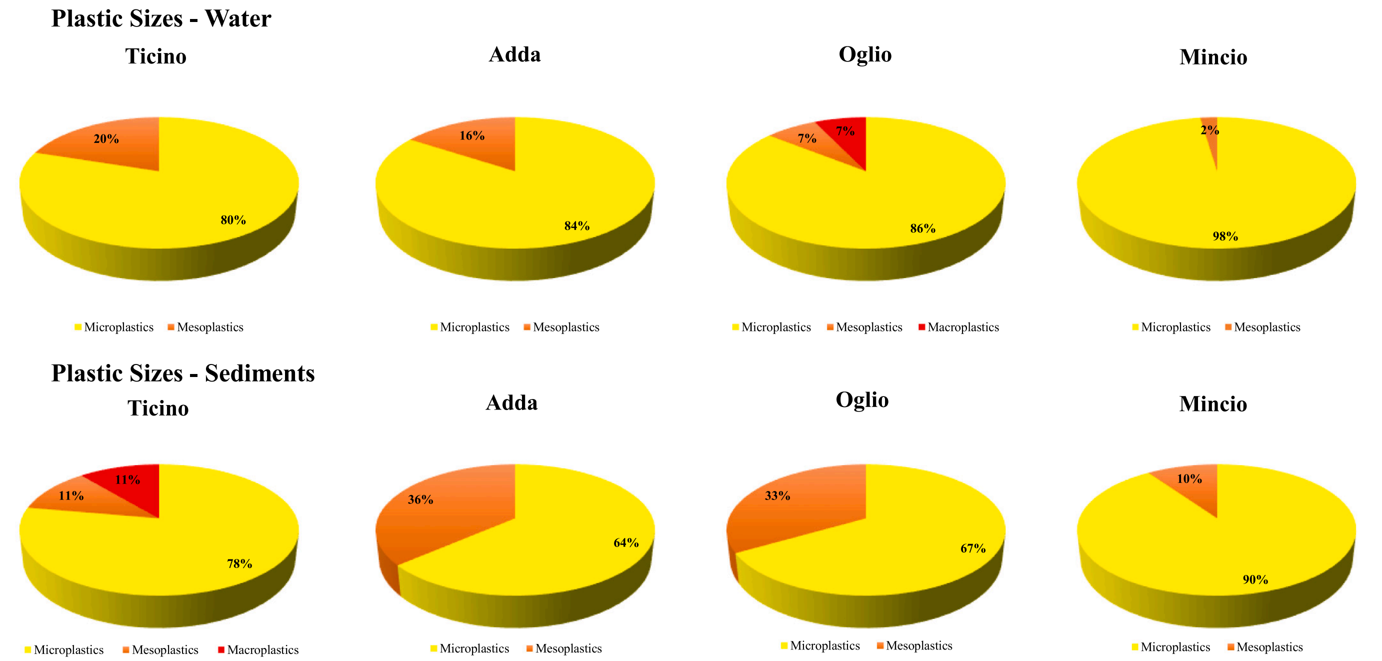

Fig. 3. Plastic sizes (%) detected in water and sediments of the selected rivers.

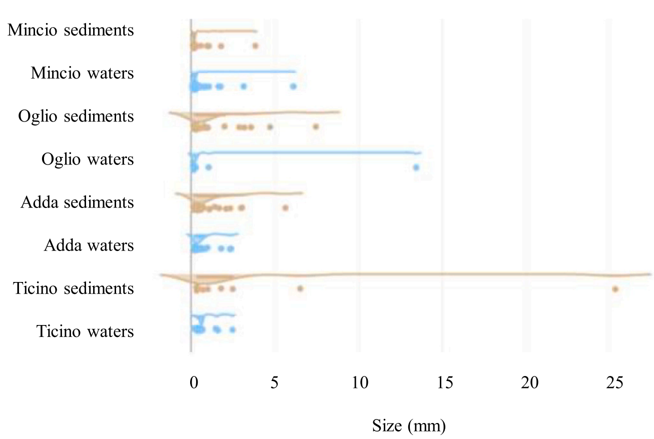

Fig. 4. Size distribution (raincloud plot; the "cloud" indicates the data distribution, while the "rain" the size raw data reported in Table S3) of plastics in water and sediments of the selected rivers.

Plastic characterization, in both waters and sediments, was made up mainly of microplastics, with percentages of 86 % and 67 %, respectively, and a similar size distribution (Figs. 3 and 4). In a different manner to the rivers describe above, in the waters we detected a high amount of pellets (86 %; Fig. 5), all constituted by PS (Fig. 6), followed by fibers (14 %). The situation was completely different in the sediments, which presented a similar contamination by plastics to Ticino and Adda. Indeed, fibers (76 %) were the main polymer, followed by fragments (24 %; Fig. 5). The main detected fibers were of PEST (81 %; Fig. 6).

Transparent was the main colour in waters (86 %), while in sediments we detected black (29 %) followed by blue plastics (24 %).

3.3.4. *Mincio River*

In Mincio River we observed the highest amount of particles between the selected water courses, despite no statistically significant differences among rivers were observed (Fig. 2A, B).

In Mincio waters we detected a total of 300 particles in three replicates, with a ratio of 221 plastics (74 %; Table S3), 27 particles with natural origin (9 %), and 52 unknown (17 %). In Mincio sediments we analyzed 113 particles, with 31 plastics (27 %; Table S3), 80 with natural origin (71 %) and 2 unknown (2 %). Therefore, plastic concentration ranged from 62.9 ± 53.9 plastics/m^3 (Table 1 and Fig. 2A), considering the filtered volume of 1.17 m^3 (0.06289 plastics/kg; Table 1), to 26.5 ± 13.3 plastics/kg sediment d.w. (Table 2 and Fig. 2B). We did not observe significant differences in plastic content between Mincio waters and sediments (Fig. 2C).

Mincio River showed, in both waters and sediments, mainly microplastics, with percentages of 98 % and 90 %, respectively, and a similar size distribution (Figs. 3 and 4). Plastic characterization, as in the water of Oglio River, showed a high pellet percentage both in waters (89 %) and sediments (77 %; Fig. 5). Pellets were mainly constituted by PS (100 % in waters and 96 % in sediments; Fig. 6), followed by 4 % styrene butadiene (SBR) pellets in sediments. All detected fibers in sediments (16 %; Fig. 5) were composed by PEST (Fig. 6).

Colour distribution of plastics was very similar between the two matrices, but different compared to the other rivers (except to Oglio waters), due to the high transparent pellet abundance (90 % in waters and 84 % in sediments).

4. Discussion

4.1. *Characteristics of plastic contamination*

The analysis of plastic contamination among the sampled rivers revealed some variations both in composition and in concentration. We will start first with the description of the qualitative characteristics of the plastic pollution detected, as the quantitative analysis deserves a subsequent expansion based on the comparison with other rivers worldwide.

Concerning the qualitative characteristics of plastics, microplastics were the main detected size in all rivers (Figs. 3 and 4), with highest values (98 %) in Mincio River waters. In addition, with the exception for Mincio matrices and Oglio River waters, PEST fibers were consistently the main detected plastic, although other synthetic polymers used in textile, as PAK, were observed (Fig. 6). Therefore, Ticino, Adda, and partially Oglio Rivers, had the same domestic (and secondary) plastic

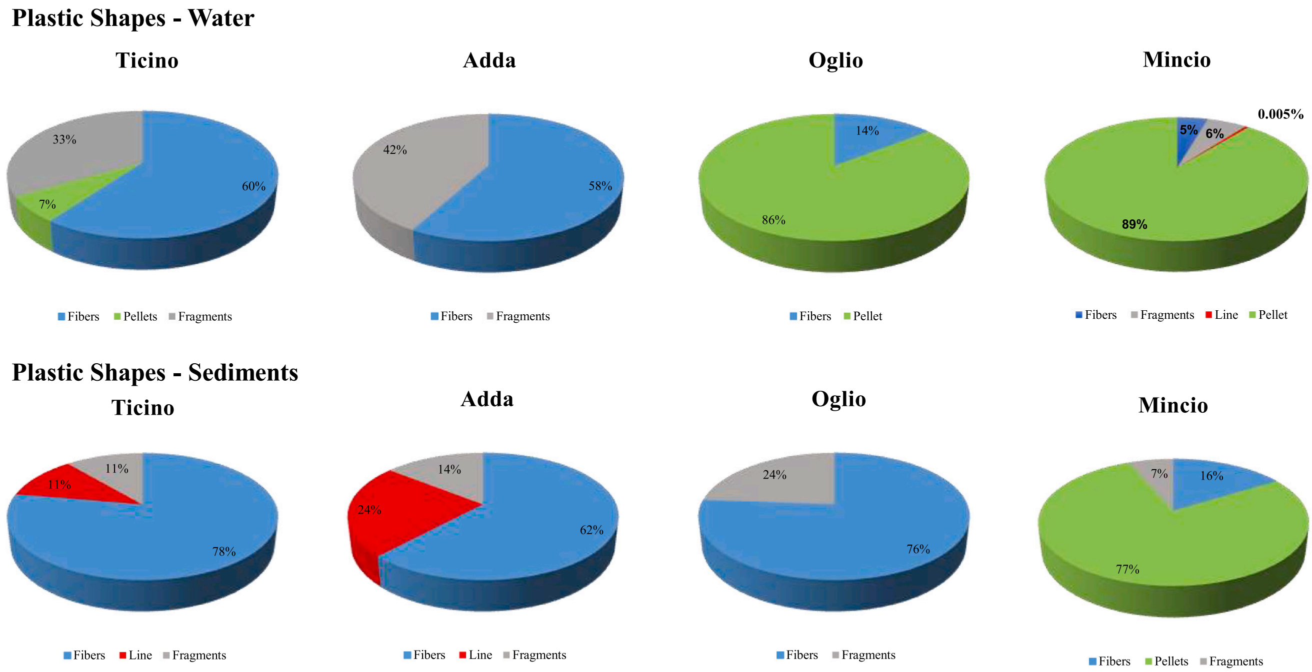

Fig. 5. Plastic shapes (%) detected in waters and sediments of the selected rivers.

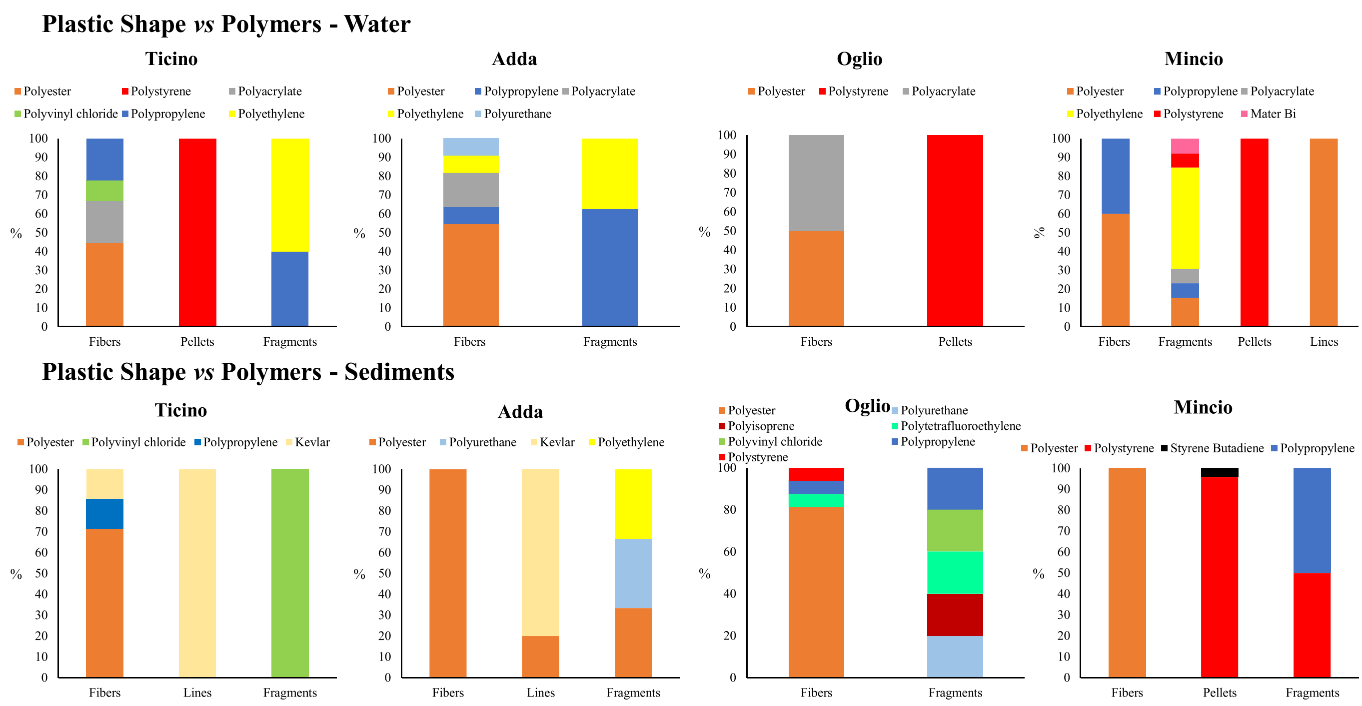

Fig. 6. Different shapes vs polymers (%) of plastics detected in water and sediments of selected rivers.

contamination. One of the main sources of synthetics fibers is the washing of synthetic clothes, as suggested by Hazlehurst et al. (2023), which reported that domestic laundering discharged from 6490 to 87,165 tons/year of fibers in aquatic ecosystems worldwide, due to the incomplete fiber removal by WWTPs (Magni et al., 2019). In addition, it is important to consider that PEST fibers can reach the aquatic environments also by atmospheric deposition, since a release of 347 ± 102 microfiber/g of 100 % PEST clothes during a simulation of normal daily activities was observed (De Falco et al., 2020). However, another secondary contamination by PE and PP fragments was detected, especially in Adda and Ticino River waters. This suggests a domestic origin of plastics in these rivers, but also a significant contribution from macroplastic fragmentation in the environment. In this context, the study of He et al. (2019) just reported that PE and PP were the main polymers in municipal solid waste landfills and 99 % microplastics in the environment derived from the fragmentation of macroplastics made of these polymers.

Our survey highlighted a completely different origin of plastic pollution in Mincio River waters and sediments, as well as in Oglio River waters: they were mainly impacted by a primary contamination represented by transparent PS pellets (Figs. 5, 6). These particles showed similar sizes in the two matrices (all pellets were 100 % microplastics), with a mean value of 0.18 ± 0.05 mm in Oglio River waters and 0.17 ± 0.05 mm and 0.19 ± 0.05 mm in Mincio River sediments and waters, respectively. Although these sizes could be mainly attributable to beads used as abrasive agents in personal care products (PCPs), this origin should be excluded as PCPs containing microplastics were banned in Italy since 2020. More realistically, this particular shape is used in industrial activities to produce raw material which is then remelted to obtain the commercial plastic objects. Indeed, the PS pellets are one of the main used thermoplastics, normally as pre-expanded or expanded PS (Howard, 1993) which can be released in freshwaters during both manufacturing and transport (Hu et al., 2023). Confirming the frequent presence of these PS pellets in freshwaters, they were detected in different monitoring campaigns also in another Po River tributary (Lambro River) passing through heavily industrialized areas, which resulted high impacted by these kind of plastics (Magni et al., 2021, 2022b; Binelli et al., 2022). Also the study conducted by Corcoran et al. (2020) on the Great Lake beaches in North America pointed out the high presence of these plastic pellets, whose concentration was positively correlated with the greater numbers of plastic industries.

The advantage of analyzing by the µFT-IR every single particle and not resorting to the increasingly popular partial analysis of the sample, is demonstrated by the fact of being able to detect even rare polymers, which are difficult to characterize with an incomplete instrumental analysis. In our case, indeed, we were able to reveal Kevlar fibers and lines at not negligible percentages in the Adda (80 % lines) and Ticino (100 % lines and 14 % fibers) sediments, where this polymer tends to move and get trapped due to its high-density (1.44 g/cm^3; Miller et al., 2021). This aramid plastic is very resistant to the tensile strength and it is used in several applications as personal protective equipment, bicycle tires, rope, cable, conduit, brakes, expansion joints and hoses, smartphones and fishing lines (Saddam Hossain et al., 2018). In the same manner the SBR, another rare polymer, was detected in the sediments of Mincio as pellets (4 %). This plastic is used in the production of tire rubbers and, when in fragment shape, it can be considered a potential

Table 3

Comparison of plastic contamination levels, in both waters and sediments, in several rivers around the world. The following studies are cited in the Table: Winkler et al. (2022), Magni et al. (2021), Binelli et al. (2022), Magni et al. (2022b), Magni and Sbarberi (2022), Campanale et al. (2020), Munari et al. (2021), Fiore et al. (2022), Pihel et al. (2019), Ghinassi et al. (2023), Rimondi et al. (2022), Guerranti et al. (2017), Scherer et al. (2020), Klein et al. (2015), Simon-Sánchez et al. (2019), Matjašič et al. (2023), Constant et al. (2020), Horton et al. (2017), Blankson et al. (2022), Nel et al. (2018), Crew et al. (2020), He et al. (2020), Ding et al. (2019), Huang et al. (2021), Lin et al. (2018), Wang et al. (2018), Sarkar et al. (2019), Alam et al. (2019), Kieu-Le et al. (2023), Battulga et al. (2020), Hwi et al. (2020).

River	Country	Plastics in water (plastics/m^3)	Sampling mesh (µm)	Extraction method (Water)	Plastics in sediments	Extraction Method (Sediments)	Analytical method	Reference
Ticino	Italy	0.86 ± 0.45	100	NaCl	6.75 ± 4.50 plastics/kg d.w.	$ZnCl_2$	µFT-IR	Current study
Adda	Italy	3.61 ± 2.31	100	NaCl	17.38 ± 9.87 plastics/kg d.w.	$ZnCl_2$	µFT-IR	Current study
Oglio	Italy	4.99 ± 2.69	100	NaCl	17.38 ± 8.60 plastics/kg d.w.	$ZnCl_2$	µFT-IR	Current study
Mincio	Italy	62.89 ± 53.90	100	NaCl	26.50 ± 13.25 plastics/kg d.w.	$ZnCl_2$	µFT-IR	Current study
Ticino	Italy	33.3	60	NaCl	11 plastics/kg d.w.	NaCl	µFT-IR	Winkler et al., 2022
Lambro	Italy	0.4 - 14.3	300	NaCl			µFT-IR	Magni et al., 2021
Lambro	Italy	71 - 388	100	NaCl			µFT-IR	Binelli et al., 2022
Lambro	Italy	89 - 2,070	100	NaCl			µFT-IR	Magni et al., 2022b
Lambro	Italy				53.3 ± 16.1 plastics/kg w.w.	$ZnCl_2$	µFT-IR	Magni and Sbarberi, 2022
Olona	Italy	555	100	NaCl			µFT-IR	Binelli et al., 2022
Olona	Italy	62	100	NaCl			µFT-IR	Magni et al., 2022b
Ofanto	Italy	0.9 - 13	333	NaCl			Py–GC/MS	Campanale et al., 2020
Po	Italy	0.29 - 3.47	330	Filtration with Sieves			FT-IR	Munari et al., 2021
Po	Italy	1.89 - 8.22	333	Filtration with Sieves			Imaging analysis	Fiore et al., 2022
Po Delta (beaches)	Italy				2.92 - 3.30 plastics/kg d.w.	$ZnCl_2$	µFT-IR	Piehl et al., 2019
Arno	Italy				440 - 5,680 plastics/kg	$3Na_2WO_4 \cdot 9WO_3 \cdot H_2O$	Raman	Ghinassi et al., 2023
Mugnone	Italy	833 - 16,000	1.6	NaCl	500 - 1,540 plastics/kg d.w.	NaCl	FT-IR	Rimondi et al., 2022
Ombrone	Italy				45 - 1,069 plastics/kg d.w.	NaCl	Visual	Guerranti et al., 2017
Elbe	Germany	5.57	150	$CHKO_2$	3,350 plastics/kg d.w.	$ZnCl_2$	FT-IR and Py–GC/MS	Scherer et al., 2020
Rhine	Germany				228 - 3,763 particles/kg	NaCl	µFT-IR	Klein et al., 2015
Ebro	Spain	1.95 - 4.3	5	Directly Filtered	2,052 plastics/kg d.w.	NaCl	µFT-IR	Simon-Sánchez et al., 2019
Ljubljanica	Slovenia	31	150	Directly Filtered	23 plastics/kg	NaCl	µFT-IR	Matjašič et al., 2023
Kamniška Bistrica	Slovenia	59	150	Directly Filtered	22 plastics/kg	NaCl	µFT-IR	Matjašič et al., 2023
Têt	France	42	333	Directly Filtered	258 plastics/kg	NaCl	µFT-IR	Constant et al., 2020
Thames basin	UK				185 - 660 plastics/kg	$ZnCl_2$	Raman	Horton et al., 2017
Densu	Ghana	100,000	1.2	Directly Filtered	388 plastics/kg d.w.	NaCl	Visual	Blankson et al., 2022
Bloukrans River	South Africa				6.3 - 160.1 plastics/kg d.w.	Not specified	Visual	Nel et al., 2018
St. Lawrence	Canada	120 - 160	100	Canola Oil	65 - 7,561 plastics/kg d.w.	Canola Oil	Visual	Crew et al., 2020
Brisbane	Australia				10 - 520 plastics/kg d.w.	$ZnCl_2$	µFT-IR	He et al., 2020
Wei	China	3,670 - 10,700	75	NaCl	360 - 1,320 plastics/kg	NaCl	SEM	Ding et al., 2019
West	China	2,990 - 9,870	75	Directly Filtered	2,560 - 10,240 plastics/kg d.w.	Directly Filtered	µFT-IR	Huang et al., 2021
Pearl	China	379 – 7,924	20	NaCl	80 - 9,597 plastics/kg d.w.	NaCl	µFT-IR	Lin et al., 2018
Wen-Rui Tang	China				32,947 plastics/kg d.w.	$ZnCl_2$	µFT-IR	Wang et al., 2018
Ganga	India				99.27 - 409.86 plastics/kg d.w.	$ZnCl_2$	µFT-IR	Sarkar et al., 2019
Ciwalengke	Indonesia	5,850	1.2	Directly Filtered	30.3 plastics/kg d.w.	NaCl	Raman	Alam et al., 2019
Mekong	Vietnam	53.8	300	NaCl	6,000 plastics/kg d.w.	NaCl	µFT-IR	Kieu-Le., 2023
Tuul	Mongolia				603 plastics/kg	$3Na_2WO_4 \cdot 9WO_3 \cdot H_2O$	µFT-IR	Battulga et al., 2020
Sungai Dungun	Malaysia	22.8 - 300.8	200	Directly Filtered			FT-IR	Hwi et al., 2020

marker of contamination by Tire Road Wear Particles (TRWPs), originated at the asphalt interface during the activity of transport means. Indeed, due to the presence of carbon black in tires, the infrared spectroscopy, normally used in the monitoring of conventional plastics, is not suitable for the detection of tire particles (Corami et al., 2022; Magni et al., 2022a). Also the fragment of polyisoprene (IR), used in the tire rubber mixture and detected in the Oglio sediments (20 % of fragments), can be related to TRWPs (Irifune et al., 2023).

From a quantitative point of view, Mincio River exhibited the highest number of plastics, both in sediments and in waters (Tables 1, 2), suggesting it was subjected to a greater input of plastics, despite the lack of significant differences with the other rivers (Fig. 2A, B and C). This characteristic was very peculiar and unexpected, considering that Mincio River is shorter than the other monitored rivers, and receives the lowest number of civil WWTP effluents (49). Coherently, while in the other rivers the contamination had domestic origin, in Mincio River mainly pellets from industrial sources were found. On the contrary, Ticino was less contaminated, while Adda and Oglio showed a comparable plastic pollution, highlighting an increasing plastic pollution along the west-east direction toward the Adriatic Sea (Fig. 1).

4.2. Comparison with other rivers worldwide

Table 3 reported a comparison between plastics found in waters and sediments in different rivers worldwide. Noteworthy, the sampling and plastic extraction/characterization methods are very heterogeneous, and harmonization of these techniques should be adopted in future studies to make easier the comparisons (Lu et al., 2021). Anyway, the studied rivers are among those with the lowest plastic concentrations, both for waters and sediments, also for the highly contaminated Mincio River in which a comparable plastic concentration to other Italian and European rivers was found (Table 3). Considering other Italian water courses, Mugnone River showed the greatest amount of plastics in water (833–16,000 plastics/m^3) and seems to be the European river most impacted by floating plastics, at least as regards the bibliographic data found, even exceeding the highest levels found in some Chinese rivers, such as Wei River (up to 10,700 plastics/m^3), West River (up to 9870 plastics/m^3) and Pearl River (up to 7924 plastics/m^3), but not reaching the dramatic values found in Densu River (Ghana; 100,000 plastics/m^3) as shown in Table 3.

We need to investigate the case of the low contamination detected in the Ticino River that was also monitored in a previous study (Winkler et al., 2022) reporting a higher contamination in water, but a similar plastic contamination in sediments, despite the use of different hypersaline solution in the extraction protocol (Table 3). The different amount of plastics in water could be influenced by the different mesh size used in the previous study (sampled with 60 μm mesh), even if for such comparisons it is always necessary to consider the great variability due to the season or to the meteorological and hydrological conditions which cause the concentration of plastics in the water to vary even daily.

Concerning sediments, Arno River presented the highest plastic contamination in Italy (up to 5680 plastics/kg; Ghinassi et al., 2023), although about 6 times lower than levels detected in the Wen-Rui Tang River (China) which represents the highest polluted water course worldwide, at least for sediments, with a concentration of 32,947 plastics/kg d.w. (Table 3).

One of the most important aspects reported in Table 3 is the extremely high sediment contamination compared to waters. Coherently, in our study the level of plastics in sediments reached the higher values of 4 orders of magnitude compared to waters, with significant differences ($p < 0.05$) for Adda and Oglio Rivers (Fig. 2C). The most striking difference is the one of Elbe River where sediments showed an average plastic concentration even 600,000-fold higher than waters (Scherer et al., 2020; Table 3). This aspect points out that sediments act as sink for plastic pollution, as recently suggested by He et al. (2021) and van Emmerik et al. (2022a). On the other hand, this is not surprising considering not only the capability of high-density polymers to sink to the bottom of rivers, but also because plastics which should float, due to their density lower than water, are also commonly found in sediments due to biofouling. Notwithstanding there could be a great capacity to retain plastic particles that end up on the bottom, especially in the case of soft sediments, we did not observe any relationship between sediment characteristics (grain size in particular) and plastic retention (Table S2). The lowest plastic concentrations detected in Ticino sediments (Table 2) were not significantly correlated to the highest gravel percentage (49 %; Table S1), although spaces in a coarse matrix could promote plastic transport by water flow. Similarly, the high plastic abundance in Mincio sediments (Table 2) was not significantly correlated to the highest silts and fine sand percentage (about 7 % and 9 %, respectively; Table S1). Based on this evidence, and considering that often waters and sediments are not analyzed together, as done in our study, a key question arises: what matrix proved to enable a reliable plastic characterization and to tell an inspiring story of plastic pollution in a river stretch?

4.3. Matrix selection, implications for monitoring and ecological relevance

To answer this question, it is necessary to evaluate the advantages and drawbacks of the sampling and analysis of the two river compartments that are summarized in Table 4. As regard sampling, the two matrices show many differences because sediment sampling is immediate and not time-consuming, but Van Veen grab does not work properly in deep rivers and in case of pebbles (Adomat et al., 2022). On the contrary, plankton net to collect floating plastics allows the sampling of all water courses, independently by depth, but the amount and size of collected plastics is strongly dependent by the net mesh size and, to a lesser extent, by the sampling time. The use of meshes smaller than 100 μm allows the sampling of a 4 times higher number of plastics than the standard 300–330 μm mesh (Converton et al., 2019; Binelli et al., 2022).

Regarding the sample treatment, it is evident that the main difference between the studies available concerns the type of hypersaline solution used for plastic extraction (Table 3). Indeed, as previously mentioned, $ZnCl_2$ is highly recommended in the separation of high-density polymers by sediments (Mattson et al., 2022), but many authors still used the NaCl for the treatment of this matrix due to its lower cost and *non*-hazardousness. This makes data comparison impracticable because NaCl underestimates plastic separation in sediments. As reported by Magni and Sbarberi (2022), a significant difference ($p < 0.05$) in plastic extraction by NaCl compared to $ZnCl_2$ was observed, with 8.3 ± 10.4 plastics/kg sediments w.w. extracted by NaCl solution and 53.3 ± 16.1 plastics/kg w.w. extracted by $ZnCl_2$ from Lambro River sediments.

Another aspect that needs attention is the visual sorting, since in sediments it is complex to discriminate plastics from the numerous interferent materials, even if we have on the filter fewer plastic items than water (Table 3). On the contrary, despite an easier discrimination of plastics from organic matter in waters, the high amount of particles found is time-consuming to perform a reliable visual sorting.

Therefore, visual sorting should be followed by an analytical characterization of the total sorted particles since visual inspection alone or analytical characterization of only a sub-sample tend to overestimate plastic contamination due to the high percentage of potential plastics of natural origin (e.g. cellulose fibers; see Section 3.3). Visual inspection alone does not provide qualitative data, which is crucial in sample characterization and in understanding contamination sources. Moreover, the partial analytical characterization of plastics collected by visual sorting often prevents the detection of rare synthetic polymers which can be very useful as markers of contamination type, possibly also tracing its origin. Furthermore, this partial characterization should not simply be done on any sub-sample, supposing then that it is representative of the whole sample, but should analyze the particles taking into

Table 4
Pros and Cons in sampling, sample processes and outcomes for sediment and water analysis in the context of plastic monitoring.

	Sediments - pros	Sediments - cons	Waters - pros	Waters - cons
Samplings	Not time-consuming	Grab closure challenging with stony sediments Hard in deep streams	Applicable in any water course Not depth dependent	Plastic collection depends on the sampling time and the mesh size
Plastics extraction	$ZnCl_2$ solution extracts also high-density polymers	$ZnCl_2$ solution is expensive and corrosive	NaCl solution is cheaper and harmless	NaCl solution extract only low-density polymers
Visual sorting	In general, few number of particles *per* filter	Many interferent materials on the filter	Easy visual discrimination of plastics to organic matter	Complexity in the visual sorting due to the high number of particles *per* filter
Contamination realism	Historic plastic contamination Slight dependence on hydrological regime	No plastic flux description	Plastic flux description toward the receiving water body	Strictly dependent by seasonality and hydrological regime Description of plastic quantity during the sampling time
Types of polymers	Both high- and low-density polymer occurrence		High variety of polymers of recent contamination origin	Only low-density polymers

account their representativeness in the sample at least in terms of shape and polymer. However, the only reason for this partial analyses is the fact that they are less time-consuming than the analysis of the entire set of plastics selected through the visual sorting.

Lastly, it is clear that both the number and type of plastics are different into the selected environmental matrices. As reported in Table 3, as well as observed in Ticino, Adda, Oglio and Mincio Rivers, sediments have a higher number of plastics and contain both high- and low-density polymers. This matrix is not dependent, unlike water, by the hydrological regime but it is closely influenced by the extreme meteorological events (van Emmerik et al., 2022b). In addition, sediments tell a long history of plastic contamination of the water course, but it is impossible to know the plastic flux of the river trait and to the receiving water basin. Water, instead, despite contains a smaller number of plastics, presents a heterogeneous variety of polymers that describe the recent contamination, and its analysis allows to assess the plastic flux toward the receiving water body. Probably for these differences, no significant covariation between the number of plastics in sediments and the respective amount in aqueous matrix was observed (Table S2). Lastly, water monitoring is strictly influenced by both the season and hydrological regime (Nakayama and Osako, 2023).

Therefore, answering the previous question, the best matrix to sample for the best picture of plastic pollution in rivers is not easy to choose and depends by the aims of the study. Surely, to assess the origin of the plastic contamination, the analysis of both sediments and waters is recommended because, as observed in our study, both matrices contain plastic particles with different polymers and shapes which indicate different sources of pollution (domestic or industrial). To understand the flux of plastics (*per* hour or day or year) in river traits and/or toward the receiving basin, water sampling should be the best technique for a routinely monitoring, even considering its quick, easy, cheap, effective analyses compared to sediment protocols. On the other hand, plastic monitoring in sediments allows to evaluate the evolution of contamination because plastics are more retained in this matrix, especially in absence of extreme hydrological events that can cause plastic drift.

5. Conclusions

The four analyzed water courses, being among the main tributaries of the Po River and acting as outflows of the four main northern large and deep lakes, showed a plastic contamination lower than those monitored in other rivers worldwide. However, the sampled rivers transport millions of cubic meters of water every day and accumulate millions of tons of sediments in their basins contributing a high plastic flow to Po River and to Adriatic Sea. The observed contamination was mainly associated to PEST fibers of domestic origin, despite a consistent industrial PS pellet contamination was measured, especially in Mincio River.

Based on the obtained results, to evaluate a reliable plastic pollution of river ecosystems, it is necessary to monitor both sediments and floating plastics because the concentration of these contaminants is different in the two environmental compartments. Sediments, indeed, provide information about the history of the plastic pollution, while waters represent a snapshot of the present plastic contamination. The choice is yours!

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CRediT authorship contribution statement

Riccardo Sbarberi: Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft. **Stefano Magni:** Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Supervision, Writing – original draft. **Angela Boggero:** Methodology, Writing – review & editing. **Camilla Della Torre:** Writing – review & editing. **Lara Nigro:** Formal analysis, Writing – review & editing. **Andrea Binelli:** Conceptualization, Funding acquisition, Project administration, Resources, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Riccardo Sbarberi reports financial support provided by Italian Ministry of University and Research (PhD fellowship).

Data availability

Data will be made available on request.

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