CAN COVID-19 PANDEMIC CHANGE PLASTIC CONTAMINATION? THE CASE STUDY OF SEVEN WATERCOURSES IN THE METROPOLITAN CITY OF MILAN (N. ITALY)

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ABSTRACT

The more or less extensive lockdowns, quarantines, smart working and the closure of numerous recreational or personal care activities due to the COVID-19 pandemic have not only heavily changed the habits and behaviors of all of us, but have also had consequences on the release of some types of pollutants. The aim of this study was to evaluate the possible changes due to the indirect effects of the pandemic in the contamination of plastic mixtures sampled in 9 watercourses of the metropolitan city of Milan (N. Italy), which is one of the major industrialized and urbanized areas in Italy. To achieve this goal, we carried out two sampling campaigns, the first one carried out in November 2019, before the arrival of the SARS-CoV-2 virus in Italy, the second in November 2020, during a severe regional lockdown that coincided with other restrictions imposed at the national level.

The main results showed a difference in contamination of plastics between the two samplings, not so much due to a quantitative variation, but certainly qualitative. We obtained non-homogeneous data with respect to changes in the number of plastics sampled in the different waterbodies, while it was evident that the plastics' contamination has shifted from a primary and industrial origin to one due to a secondary origin of the sampled plastics, linked especially to the fragmentation of common use objects, or deriving from synthetic garments.

Keywords: COVID-19 pandemic; lockdown; plastic pollution; freshwaters

1. INTRODUCTION

The pandemic due to COVID-19 is not only changing our social and working habits, but its impact in all civil and industrial activities could have indirect consequences even in fields far from the typically health ones. Indeed, lockdowns, quarantines and travel limitation may have changed the release of pollutants in different natural ecosystems, showing how a change in our way of life can have a significant impact on the environment. There are already several scientific evidence that have shown how this global pandemic has changed the contamination of some natural ecosystems. The European Space Agency (ESA) reported a reduction of 20-

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30% in February 2020, compared to the previous three years, in surface particulate matter over large parts of China in relation with the quarantine and lockdown in Wuhan and other Chinese cities (ESA, 2020). The same Agency also highlighted a decline in atmospheric nitrogen dioxide (NO_2) concentrations in Italy, particularly in the northern regions, in coincidence with the nationwide lockdown to prevent the spread of SARS-CoV-2 virus (ESA, 2020). There are now hundreds of these studies concern the changes due to the COVID-19 pandemic on the atmospheric pollutants worldwide, also linked to climate change (Bashir et al., 2020; Bilal et al., 2020; Mahato et al., 2020; Stratoulias et al., 2020; Gaubert et al., 2021). Instead, doing a search on Web of Science (WOS) by entering the terms "COVID-19" and "water pollution" as topics, we found only a percentage of 14% in comparison with the search with “air pollution”. The percentage drops to 0.5% when looking for papers related to changes in plastic pollution in rivers as a result of the COVID-19 pandemic (Hu et al., 2021; Robin et al., 2021; Vaid et al., 2021; Wu et al., 2022). This is amazing for several reasons: 1) rivers collect most of plastics from industrial wastes and from the civil wastewater treatment plants (WWTPs), as evidenced by the fact that 80% of global ocean plastics arise from land-based sources (Li et al., 2016); 2) lockdowns and quarantines have forced and continue to constrain many people to stay at home, changing their habits that can impact in different way to plastic release, such as those related to cooking, sport activity and cloth washing; 3) the partial or definitive closure of various industrial activities related to plastic uses, which can decrease the release of polymers of primary origin in watercourses; 4) the enormous increase in the use of personal protective equipment (PPE) made of plastic, such as facemasks, gloves, protective medical suits, hand-sanitizer bottles, medical test kits, most of which are single-use products that can be incorrectly disposed or, worse, left around in the environment. A recent estimate made by Benson et al. (2021) showed that China and India are the two countries in which the facemasks are most discarded, with values of over 700 million/day for the first country and just under 400 million/day for the second. Turning to the European situation, the country with the largest number of discarded facemasks is Russia, followed by Germany, United Kingdom, France, and Italy which ranks fifth in Europe with over 33 million/day facemasks discarded (Benson et al., 2021). The potential danger for aquatic environments and the organisms living in them due to incorrect disposal of the facemasks is shown by a recent study that has pointed out how a standard facemask can release at least 47 microplastic fibers per day (Dissanayake et al., 2021).

If the huge increase in the use of PPE to tackle the SARS-CoV-2 virus transmission can have an impact in the short and medium term in increasing the quantity of plastics that ends up in the environment and/or modifying the polymeric composition, as well as the size and shape of plastic debris, another aspect that should not be underestimated is related to changes in social and working habits that are forcing people to reduce interpersonal contacts and to stay more at home. These new behaviors, as the wide use of smart working, are often favored by central governments and by companies themselves, and they could have a direct effect on the release of plastics in the environment mainly in the urban areas. This effect is difficult to predict because less plastics could be produced by the food containers of restaurants and fastfood, since people tend to cook more at home, but this could be compensated by a greater use of food delivery whose products are often contained in single-use plastic containers. Another variable is due to the closure of gyms and sports centers for many months, which has obligated people to play sports in parks, lawns or even in streets, resulting in a greater likelihood of plastic fibers and fragments being released from technical clothing and shoes.

In this context, the goal of our study was to evaluate the effect linked to these changes imposed by the pandemic condition, which unfortunately still affects our life, on the possible modification of plastic contamination in some watercourses within the metropolitan city of Milan (N. Italy), where almost 33% of the population of the Lombardy Region and 5.5% of the Italian population live, as well as 6.6% of Italian companies are located (www.cittametropolitana.mi.it).

The achievement of this objective was possible because in a period (November 2019) immediately preceding the start of the COVID-19 pandemic in Italy we had already carried out a monitoring campaign to evaluate the qualitative and quantitative characteristics of plastic mixtures collected in 9 of the main waterbodies that enter or leave Milan, whose results are in-depth explained in a previous recent article (Binelli et al., 2022).

Therefore, we carried out a second monitoring campaign in the same watercourses and sampling stations, without modifying in any way the sampling and processing procedures, in a period (November 2020) characterized by the division of the Italian regions into three different zones (yellow, orange and red) defined by 21 different pandemic parameters (De Leo and Araújo, 2021 and citations therein). In the period in which the second sampling was carried out, Lombardy was in the red zone, characterized by many severe limitations which were added to the other restrictions of national significance, such as the prohibition of any movement within the region except in cases of necessity and urgency, closure for shops retail with the exception of foodstuffs, pharmacies and newsstands, closure of pubs and restaurants, suspension of sports activities including those carried out in outdoor sports centers, school activities in attendance only for kindergartens, primary and middle schools, limitation of the presence of public personnel in the workplace to ensure only the activities that cannot be postponed. This situation represented a sort of regional lockdown, following the complete national lockdown that took place in February-April 2020 when the SARS-CoV-2 virus had arrived in Italy.

The sampling of the plastic mixtures was carried out using 2 twin plankton nets (100 μm mesh), the first of which collected the plastic mixtures to be subjected to the qualitative-quantitative analysis by means of a Fourier-Transform Infrared spectrometer coupled with an optical microscope (μFT-IR), while the 9 plastic mixtures collected in the second net were used for the evaluation of their possible ecotoxicological effects (data not shown).

To our knowledge, this study is the first comparison carried out in riverine environments for the evaluation of possible changes in the characteristics of plastic contamination due to the measures taken to decrease the spread of the SARS-CoV-2 virus and to their direct and indirect consequences on social and working habits of a large human community, such as the one living in the metropolitan city of Milan.

2. MATERIALS AND METHODS

2.1 Study area

Among the numerous rivers and artificial canals that cross the metropolitan city of Milan, we have chosen the 7 most important ones, apart from the Seveso River because in the two sampling periods it was dry for the city part of its course due to the normal routine maintenance interventions always provided for the autumn months.

Figure 1 shows the complexity of the watershed of Milan and the 9 different sampling stations located in the 7 waterbodies whose hydrographic characteristics have already been described in our previous paper (Binelli et al., 2022). As can be seen, we have chosen sampling points located both on the watercourses entering and leaving Milan to also evaluate the possible impact of city activities on the release of plastic in these waterbodies.

It should be noted that even if they are not particularly large, they are still part of the watershed of the Po River, the main Italian watercourse. It is possible to divide the selected waterbodies into different river systems which are briefly described.

2.1.1 River Olona system

It is a natural river 60 km long and crosses a highly anthropized and industrialized area located north-west of Milan. It continues sealed in the city, while its diverter branches off from the natural course, tangling the suburbs to the southwest and collecting the waters coming from the north-west spillway, that defends the metropolitan city from the risk of floods due to waterbodies located north of Milan (www.regione.lombardia.it). The waters of the diverter flow south of Milan back into the Olona River, which in turn flows into the Po River. We carried out the sampling directly on the natural course of the Olona River (OLO; 45.510418, 9.085068) just before its entry into Milan and on the Olona diverter (OD; 45.447052, 9.114980), leaving the metropolitan city (Fig. 1).

2.1.2 River Lambro system

This river, also of natural origin, is the one with the most linear course in Milan, as it is about 130 km long and crosses one of the most Italian anthropized and industrialized areas before entering and leaving Milan without any kind of diverter, spillway or effluents. Along its course, which also flows directly in the Po River, it collects the wastewaters of about thirty WWTPs, in addition to the waters of 27 tributaries (www.regione.lombardia.it). We have chosen a sampling station located at the entrance to Milan (Lambro River Upstream; LAU; 45.512222, 9.259377), to highlight the plastic pollution coming from the area heavily impacted by the numerous industrial and anthropogenic activities located at north of the metropolitan city, and a sampling site located just before the river exit from Milan (Lambro River Downstream; LAD; 45.454564, 9.258776) to check if city activities can modify plastic contamination (Fig. 1).

2.1.3 Navigli canal system

The Lombard Navigli is a fascinating and complex system of artificial canals, once used for the transport of goods, which was fundamental in the past for the economic development of Milan both in terms of trade and as a water resource for fields surrounding the metropolitan city (www.naviglilive.it). Today this only function has remained, as navigation is only possible in a few sections and exclusively for tourist use. The Navigli system extends for kilometers connecting Milan to Lake Maggiore, Lake Como, the Po River, as well as the Ticino River. The Navigli system of Milan consists of 5 canals: Grande, Pavese, Bereguardo, Martesana and Paderno (www.regione.lombardia.it). Among them, we have sampled the Naviglio Grande and Pavese, which represent one a continuation of the other, and the Naviglio Martesana (Fig. 1).

The Naviglio Grande originates from Ticino River and ends in the Darsena of Milan, with a total extension of 50 km, characterized by the presence of 120 secondary irrigation branches (). The Naviglio Pavese originates from the Darsena of Milan (Fig.1), which today represents one of the city's major tourist areas and, after a 33 km long river course, it flows into the Ticino River, the main Lombard tributary of the Po River.

The chosen sampling stations (Fig.1) are placed just before entering Milan (Naviglio Grande Canal; NGC; 45.430009, 9.104733) to evaluate the contribution in terms of plastics from the north-western agricultural area of Milan, and in the southern suburbs, just before its exit from the metropolitan city (Naviglio Pavese Canal; NPC; 45.437823, 9.174713).

2.1.4 Martesana-Redefossi system

This is another system consisting of two small artificial canals connected directly to each other in the center of Milan (Fig.1). The Martesana Canal, with a vocation now exclusively for irrigation, arises from the right bank of the Adda River, a tributary of the Po River, and runs outdoors for about 38 km up to Milan, where it is sealed in the north-east area of the city up to reach the old town, where it generates the Redefossi Canal (www.regione.lombardia.it). Normally, the sealed section of the Martesana Canal would also collect the waters of the Seveso River which, as previously mentioned, was dry for maintenance work in both sampling periods.

Redefossi Canal is a small waterbody (18 km of length), representing the artificial continuation of Martesana Canal, which comes out always sealed in the south-eastern area of Milan until it flows into the River Lambro through a diverter that has currently replaced the old riverbed. The two sampling stations were placed one at the entrance of the Martesana Canal in Milan (Martesana Canal; MAR; 45.509555, 9.247448), the other on the Redefossi diverter (RDF; 45.407846, 9.289111) located close to the outlet to Lambro River (Fig. 1).

2.1.5 Vettabbia Canal

It is the only waterbody that does not belong to any specific system, as it is a canal that originates in the subsoil of the old town and crosses the city for a long stretch in a southeasterly direction, becoming the longest canal in Milan, after the Naviglio Grande and Naviglio Pavese. It finally flows to the old riverbed of Redefossi Canal just before the outlet to Lambro River (Fig. 1). Its interest is mainly linked to the fact that it collects the outlet from the largest WWTP in Milan, located in the south-eastern outskirts of the city (Fig. 1) and which treats the wastewaters of about 1,250,000 inhabitants. Consequently, to assess the release of plastics derived from domestic activities, the sampling station (VET; 45.417337, 9.236230) was placed 2 km downstream of the WWTP sewer.

2.2 *Plastic sampling*

We performed the plastic sampling in November 2020. All samplings, in the different water bodies, were conducted in the same week, and the related water course systems were sampled in the same day. This aspect allows to avoid meteorological and hydrological changes, which can affect the plastic content in selected matrices. The floating plastics were collected with two twin plankton nets (100 µm mesh; Scubla S.r.l., Italy), equipped with a flowmeter (Model 2030R, General Oceanics Inc., USA), dropped by bridges for 15 min in the center of selected water courses. The plastics collected by the first net were used for the monitoring activity, while the materials from the second net were used for the ecotoxicological evaluation (data not shown). After the sampling, to recover plastics, each net was washed with 500 mL of sodium chloride (NaCl) hypersaline solution (density of 1.2 g/cm^3), and the collected material was stored at 4 °C in glass bottles with a metal cap (Binelli et al., 2022; Magni et al., 2019; 2021).

2.3 *Plastic quantification and characterization*

The NaCl hypersaline solution allows the density separation of floating plastics from the huge amount of organic matter. The plastics in the supernatant of each sample were filtered on cellulose nitrate membrane filters (8 µm mesh; Sartorius™ 50 mm) using a vacuum pump. Obtained filters were washed with ultrapure water, using a vacuum pump, and the traces of organic matter were digested with 15% v/v hydrogen peroxide (H_2O_2). Subsequently, the particles with a suspected plastic nature were translocated on clean filters using a stereomicroscope (visual sorting). All the plastic debris were quantified and characterized one by one in terms of polymer composition, color and shape using the µFT-IR (Spotlight 200i equipped with Spectrum Two, PerkinElmer) in Attenuated Total Reflectance (ATR), with 32 scans in the range 600 - 4000 cm^{-1}. The obtained infrared spectra were analyzed using the Spectrum 10 Software, maintaining only the matching scores ≥ 0.70. Regarding the plastic size, we measured this parameter, according to Hartmann et al. (2019), using the ImageJ Software on the µFT-IR images. Lastly, to monitor the fiber contamination, we processed 9 filters as blanks (Binelli et al., 2022; Magni et al., 2019, 2021).

In detail, we have identified through the visual sorting by a stereomicroscope 810 different particles with possible polymeric characteristics (Tab. 1), of which only about 55% (total number = 450) were found to be a plastic debris by the vibrational spectroscopy (Tab. 1). Table S1 shows the raw data of all the plastic debris identified by the µFT-IR.

3. RESULTS

The data obtained after the two monitoring campaigns were first validated by the negligible plastic contamination observed in the filters used as blanks for each operation performed in the laboratory. While we observed the presence of only 12 natural fibers on the blank filters examined in the 2019 campaign (Binelli et al., 2022), in the 2020 monitoring we found a total of 6 synthetic fibers in the 9 blanks, so that the only 5 fibers that matched in polymeric composition and color were eliminated from the final count of the respective samples.
Below we will describe the main differences observed for the 9 plastic mixtures sampled in the two monitoring campaigns of 2019 and 2020, while in the next chapter the thought on the possible effect linked to the COVID-19 pandemic and its consequences on the social and industrial changes on the release of plastics will be made.

3.1 Quantitative differences

Table 1 already clearly shows a first difference linked to the identification of a smaller number of plastic debris sampled in 2020 compared to the 2019 monitoring, apart from the two watercourses belonging to the Martesana system, which recorded a 2.5-fold increase in the northernmost station (MAR) and double in the one located at the exit of the metropolitan city (RDF). In the other 7 stations we have instead observed a sharp decrease in the number of plastic debris collected in 2019 and 2020, ranging from about 33% at LAD up to 91% at NGC (Table 1).
The only comparison between the total number of plastic debris provides partial information on the contamination, as it is also necessary to consider the volume of water filtered by the plankton net, which gives us the data of plastic debris concentration for each sampling station. In figure 2 it is possible to highlight a more heterogeneous situation than the previous one since, in addition to the increase already described for the Martesana system, we can see a rise of contamination also in the two sampling stations located on the Lambro River, with an increase of about 20% at LAU and even more than 80% at LAD. Conversely, evident drops in plastic debris concentration were observed at all other sampling stations. These decreases were variable between 35% (NPC) and 77% (NGC) in waterbodies with low plastic contamination, while the dramatic decrease measured at OLO was very particular since a drop of almost 90% was observed between the 2019 and 2020 monitoring campaigns (Fig. 2). Lastly, considering the measured or estimated flow of plastics in the different waterbodies (Tab. 1), we can observe the decrease of almost an order of magnitude in the flow of plastics that pass through OLO, but above all the worrying increase in the plastic passage estimated in 2020 for the sampling station placed on the Lambro River leaving the metropolitan city (LAD), with a value that exceeds 5 billion plastic debris/day (Tab. 1).

3.2 Shape differences

Figure 3 (A,B) shows a large variation in the shape of the plastic debris sampled during the 2019 campaign and that performed one year later during the regional lockdown. We can generalize these changes with a prevalence, which in some cases becomes almost total, of the

fibers over fragments, lines and especially pellets. This is mainly evident in VET and NPC, where in 2020 fibers represent more than 96% and 94% of the total plastic debris, compared to about 36% and 30% respectively, evaluated in the 2019 campaign.
We can observe as in the artificial waterbodies (Fig. 3B) the fragments, which in 2019 were the prevailing shape in all stations except MAR, were almost completely replaced by fibers in 2020. The change in the shapes of the plastic debris observed in the two rivers of natural origin is quite different (Fig. 3A), as in the two sampling sites of the Lambro River, we noticed the replacement of the pellets, found in 2019 at percentages of over 73 % at LAU and 78% at LAD, with fibers again, with percentages equal to 73% and 85%, respectively. By contrast, in the Olona River the contamination by plastic debris in the 2020 sampling is dominated by fragments, with percentages of 73% in both OLO and OD, while fibers are about a quarter of plastic debris. This replacement in shape, however, is different for the two stations since, while in 2019 pellets prevailed at OLO (about 65%), in its diverter (OD) about two third of the plastic debris was composed of fibers (Fig. 3A).

3.3 Size differences

Another parameter that changed between the pre-COVID period and the regional lockdown concerned the size of the plastic debris sampled in the 7 waterbodies. First, as reported in the methods, we followed the dimensional ranges recommended by Hartmann et al. (2019) which considers microplastics (MPs) any synthetic polymeric particle whose largest size is between 1 μm and <1 mm, mesoplastics (MSPs) between 1 mm and <10 mm and macroplastics as plastics larger than 1 cm. We consider this categorization a more clear-cut representation of the standard international nomenclature than the current terminology which considers the dimensions of the MPs between 1-5000 μm (NOAA, 2009; ECHA, 2020), resulting even less realistic as regards the biota-plastic debris relationship.
As can be seen from figure 4 (A,B) there was a generalized increase in the size of the plastics from MPs to MSPs at all sites in 2020 monitoring compared to the 2019 campaign, with the exception of OLO where the dimensional ratios remained constant with about a quarter of the debris consisting of MSPs and the rest formed by MPs. In the other sampling stations, there is a dramatic increase in MSPs compared to MPs which in some sites (NGC, MAR, RDF) do not exceed 20% of the total in 2020.

3.4 Polymeric differences

It is possible to observe also in this case some differences between the 2019 and 2020 data as regards the two rivers of natural origin and the artificial ones (Fig. 5). In fact, while in the latter there is a net increase in polyester (PEST) in 2020, with percentages ranging between 32% (RDF) and 72% (NPC), the variation in contamination is different in the Olona and Lambro Rivers. In detail, the polymer that was predominant in OLO in 2019 was the polymethyl-methacrylate (PMMA; 64%), which in 2020 was not even found in this sampling

station, having been replaced by polyethylene (PE; 73%), which made up three quarters of the entire polymeric component (Fig. 5). PE is the polymer most present in 2020 also in its diverter (OD), albeit with a slightly lower percentage (55%) than OLO, in comparison with a much more complex polymer composition observed in the 2019 campaign, in which PEST (28%) and polyamide (PA; 26%) were the most representative polymers (Fig. 5).
An even different situation can be observed in the two sites on the Lambro River, where the enormous quantity of debris in polystyrene (PS), which in 2019 made up more than 70% of the entire polymeric composition in both sampling stations, was reduced in 2020 to about 30% for LAU and only 13% for LAD, being replaced by PEST and PA which together represent about 60% of the total polymers (Fig. 5).

4. DISCUSSION

Before going into the details of the possible effect of social and industrial variations linked to the COVID-19 pandemic that may have determined a variation in plastic contamination in the metropolitan city of Milan, it is necessary to make a general consideration. Currently, studies on plastics, their environmental levels and the possible consequences on organisms and human health have a strong impact not only in the scientific community, but above all at the level of public opinion. Unfortunately, this high interest has also created incorrect approaches, as numerous monitoring papers present unsuitable experimental plans for plastic identification, based solely on visual sorting or the use of fluorescent dyes coupled with a fluorescence microscope, that still have severe limitations, such as co-staining of residual natural lipids or organic materials (e.g., wood lignin, cellulose, chitin) along with plastics (Shim et al., 2016; Stanton et al., 2019). However, in order not to overestimate the quantity of plastics detected in the environment, it is necessary to use suitable instrumentation for the qualitative and quantitative evaluation of plastic debris. As evidence of what has been said, we can highlight how, in the 2020 monitoring campaign, the plastics debris constituted only a small part of the particles detected by the μFT-IR for some sampling stations, while a high percentage of particles was found to be of natural origin, mainly cellulose. In detail, we detected a fraction of less than 50% of plastic debris for 6 sites: NGC (15% of plastics), VET (26%) MAR (31%), RDF (37%) NPC (40%) and OD (40%), while only for LAU (73%), LAD (73%) and OLO (76%) the percentage of detected plastics exceeded 50% of the particles analyzed by spectrometry. Therefore, the materials of natural origin represented a variable percentage from 24% to even 85% of the particles that with the preliminary visual sorting we had identified as possible plastic debris. Furthermore, the simple identification systems of the plastic debris described above only allow an approximate quantitative evaluation, not providing any qualitative data of the polymeric composition, which is instead fundamental to understand the origin of the contamination by plastics and to be able to perform a correct and in-depth comparison between different environments and/or sampling periods, as in the case of this study.
In any case, our experimental design still presents some apparent limitations, above all related to the fact that we have sampled in a punctiform temporal way and to the plastics collection

only for 15 minutes. To respond to these possible drawbacks, some distinctive traits should be noted: 1) the 2020 sampling was performed exactly in the same way as that of 2019 in order not to insert variables that could have invalidated the comparison; 2) sampling during the regional lockdown was very complicated, given the pandemic situation underway; 3) sampling of just 15 minutes with plankton nets of 100 µm mesh was necessary to avoid the inevitable packing of the same for longer sampling times. The experience gained in the field and the numerous tests carried out on different watercourses have actually inclined us to this short period of sampling time, absolutely sufficient to collect a significant amount of plastics, as clearly highlighted in table 1; 4) the use of 100 µm mesh is one of the most important innovations of our experimental design because it has allowed us to collect not only a greater number of plastic debris, but also of smaller dimensions (Binelli et al., 2022), such as fibers, which often do not they are sampled with the classic 300-330 µm mesh; 5) the change in the characteristics of the plastic contamination, which will be discussed later, is exactly the same for all the sampled watercourses, indicating that even if a punctiform sampling was performed, the robustness of data is sufficient, given that we analyzed hundreds of plastic debris in both years: 1487 potential plastic debris identified through the visual sorting for the 2019 campaign and 810 particles in 2020 (Table 1), then identified one by one through the µFT-iR; 6) this high number of identified plastic debris is time-consuming, consequently also limiting the use of other samplings, which would multiply the time necessary for their instrumental determination.

Therefore, even with the inevitable and intrinsic drawbacks related to the sampling of these physical contaminants, the data that will be discussed below were sufficient robust to highlight a possible effect due to the indirect effects of COVID-19 pandemic.

4.1 Quali-quantitative differences between 2019 and 2020 monitoring campaign

Moving to the main goal of our study, the difference between the contamination observed in the 9 sampling stations during the November 2019 campaign and that performed during the regional lockdown of November 2020 is absolutely evident for all the qualitative and quantitative parameters measured, as shown in the previous chapter, albeit with rather different characteristics among the watercourses.

Very interesting, even if apparently controversial, are the different trends of plastic contamination observed in the two rivers of natural origin (Fig. 1), where we observed a dramatic decrease in the concentration of plastic debris in the sampling stations located on the Olona River (OLO and OD), while the presence of plastics has clearly increased in the stretch of the Lambro River that passes through Milan, in particular in the southernmost station (LAD). This apparent discrepancy between the pollution trends observed in the Olona River and the Lambro River allows us to make a first consideration of the indirect impact that the COVID-19 pandemic has caused on the plastic contamination in the main waterbodies of the metropolitan city of Milan. Indeed, while the logical consequence of the national and regional lockdowns that unfortunately occurred between the entire 2020 in Italy would be that of a decrease in plastic contamination, our data indicate a much more complex situation,

which deserves an in-depth analysis based also on the other qualitative characteristics that we measured in the sampled plastic mixtures.
The large decrease in the concentration of plastic debris observed in particular at OLO is clearly due to a decrease in the release of primary plastics of industrial origin, as shown in figure 5 which highlights how the debris of PMMA, which made up about two thirds of the mixture sampled in the 2019, completely disappeared in 2020, being replaced by PE debris (73%), which instead is a typical plastic of secondary origin, coming from the fragmentation of numerous common use objects. The comparison between data shown in figures 4 and 7 allow us to confirm this change in the origin of the mixture of plastics present in the Olona River, as it is highlighted that in 2019 the main cause of the contamination detected at OLO it was due to pellets of PMMA, while in 2020 the mixture of plastics consisted mainly of fragments of PE. PMMA, also known as Plexiglass®, is a widely used transparent plastic material known for its applications in various markets from car windows, smartphone screens to aquariums. For the industrial applications it is available in small granules, sheet forms and just the pellets, such as those detected in 2019, which are then processed to produce objects with glass-like characteristics (clarity, brilliance, transparency, translucence).
Therefore, it is easy to hypothesize how the effect of the COVID-19 pandemic has not only caused a decrease in contamination in the Olona River, but a real change in its characteristics, passing from a purely industrial origin to a more urban and secondary one, given that the fragments of PE, revealed as the main shape at OLO, can result from the environmental degradation of films, tubes, laminates, packaging, automotive and electrical equipment, and from the old shopping bags. The reasons for this modification are to be found in the dramatic decline in the Italian industrial production which occurred due to the COVID-19 pandemic, which resulted in the partial or definitive closure of numerous industrial activities. This hypothesis is confirmed by the National Institute of Statistics (ISTAT, 2020) which underlined that 2020 closed with a decrease of 11.4% of the industrial production compared to 2019, the second worst result since the beginning of the historical series. This decline was extended to all major industrial sectors and in the case of consumer goods was the largest ever recorded.
This radical change in the different type of contamination can also be observed in many of the other sampled waterbodies, which have passed from a plastics' contamination of industrial origin to a pollution more linked to urban and household origin. In figure 5 it is possible to highlight how in 2020 a sort of simplification of contamination is observed, as most of the polymers used in specific industrial or technical applications have disappeared. For example, ethylene-vinyl acetate (EVA), used for a myriad of applications in the packaging and plastic goods industries (sealants in meat and dairy packaging structures, footwear, wire and cable insulation, pipes, toys, sport equipment, photovoltaic encapsulation, medical packaging, hot melt adhesives), which was identified in 2019 at 4 sampling stations (OLO, OD, LAD, VET), in the 2020 monitoring campaign it was never detected.
In the three stations of OLO, OD and NGC, in 2019 we also detected few fragments of a particular blend of EVA, the ethylene propylene/ethylene-vinyl acetate (EPR-EVA; Figs. 6

and 7), which has very specific industrial uses, as in the fire retarding cables used for locomotives and coaches, and in nuclear technology (Placek and Bartonícek, 2001), and which was never detected in 2020 (Fig. 5).

This situation was also found for other (co)polymers with special characteristics, such as the acrylonitrile-butadiene-styrene (ABS), an engineering thermoplastic widely used in electronic housings, auto parts, consumer products and pipe fittings, and the polyacrylic rubber (ACM), which is a synthetic elastomer mainly used in automotive seals and hoses, as well as in textiles, adhesives, and coatings (Fig. 5). Other (co)polymers with specific uses found only before the COVID-19 pandemic, even if at low percentages due to their very specific uses, were styrene-ethylene-butadiene-styrene (SEBS), ethylene propylene-diene monomer rubber (EPDM) and polyvinyl acetate (PVAc), as indicated in figure 5.

However, during the regional lockdown, all these (co)polymers used in specific industrial activities or contained in objects, equipment and instruments certainly not of common and daily use were no longer identified in the plastic mixtures sampled in the 9 different stations, while we detected the presence of polymers compatible with an origin more linked to domestic activities. Considering the data shown in Figures 4, 6 and 7, we can actually realize this dramatic change in contamination, which cannot be justified solely by the fact that the two samplings are punctiform both temporally and spatially. In general, fragments and pellets of various polymers, such as PMMA, PE, PS and polypropylene (PP), which in 2019 were predominant (Figs. 4, 7), during COVID-19 pandemic have been replaced in almost all stations by fibers (Fig. 3) mainly in PA and PEST, with lower percentages of fibers of polyacrylate (PAK) and PP, as pointed out in figure 6.

PA and PEST fibers are typically produced during domestic washings of synthetic textile fabrics (Yang et al., 2019), which are at the top of the list of sources of microfibers, accounting for about 35% of those that are released in the environment (Boucher and Friot, 2017). There are now many studies in this regard that have shown a heterogeneous, but very high release of fibers especially from washing by laundry machines. Browne et al. (2011) demonstrated how washing a single synthetic garment can release more than 1900 fibers per wash, while a release of 0.033-0.039% wet fibers from a PEST garment per washing was estimated (Dubaish and Liebezeit, 2013). Moreover, the recent paper by Cesa et al. (2020) evaluated that over 12 thousand tonnes of synthetic fibers/year would be released from washing machines worldwide. In many countries these discharges end up unaltered in waterbodies, but even where they are collected to a WWTP, fibers are not completely removed, as a percentage of MP elimination has been estimated in European WWTPs ranging from 72% to 98% (Magni et al., 2019).

4.2 The Lambro River paradox

Perhaps the most controversial feature in the comparison of the contamination between the two years remains to be discussed, namely the dramatic increase of plastic concentration noticed in the two sites located on the Lambro River, especially for LAD (Fig. 2). The plastic debris value achieved at this site (2070 plastics/m^3) is about 2 orders of magnitude lower than the plastic debris concentration recently measured in the Rhine River (The Netherlands) by Mughini-Gras et al. (2021), however obtained using a net of 10 μm mesh. Comparing the data obtained at LAD with another large European watercourse such as the Seine River (France), in which the sampling (net with 80 μm mesh) was more comparable with ours, we can realize how in the Lambro River leaving Milan we have found a concentration of plastic debris about 20 times higher than the higher level found in the main French river (Dris et al., 2017). Furthermore, the huge amount of plastics found in LAD certainly entered the Lambro River in the city circle, as LAU showed an increase in contamination of only about 20% compared to the 2019 monitoring campaign (Fig. 2).

First of all, it is necessary to dispel any doubts regarding a possible problem related to sampling, given that in table 1 it can be seen that in this station it was possible to sample only 0.1 m^3 of water, as there was an enormous amount of suspended material which blocked the flow of water into the net. Therefore, the high concentration of plastics detected at LAD could simply be due to the packing of the net, resulting in a greater collection of plastics compared to other stations. This did not happen, as we collected only 2 pellets of PS with a size less than 100 μm, which represents the mesh of the plankton net. Consequently, the high contamination detected during the regional lockdown at LAD is real, but not easy to explain because all the civil and industrial wastewaters in the area of the city crossed by the Lambro River are collected in the sewer and end up in the largest WWTP of Milan.

A possible explanation may derive from the analysis of data obtained at LAD, which showed in 2020 a percentage equal to 85% of fibers (Fig. 3), 80% of which is made up of PEST and PA in equal measure (Fig. 6), that represent two of the polymers most used in technical sportswear, the first thanks to its remarkable resistance and water-repellency capabilities, the second for its properties of breathability, sweat absorption and lightness. Our hypothesis that attempts to explain the high and worrying plastic contamination detected at LAD is that these plastic fibers derived from an increase in outdoor sports activity, which was the only one allowed during the regional lockdown, which resulted in a release of PEST and PA fibers from sportswear. This hypothesis is supported by two reasons: 1) the Lambro River, in the metropolitan stretch between the two sampling stations, crosses two large parks (Parco Lambro and Parco Forlanini), usual destinations for runners, also collecting the waters of the canals from other green areas on the outskirts of Milan and the hinterland; 2) many data analysis platforms based on sports activities have indicated a net increase in the exercise habits of people during the pandemic. For example, it was found that Italy recorded a 105% increase in the number of fitness activities in the period 9 March-14 April 2020, at the beginning of the complete national lockdown (www.garmin.com). A report conducted in April 2020 of 14,000 runners in 12 countries attests that over a third (36% globally) of them were more active than they were before the onset of the COVID-19 pandemic (www.ANSA.it). Again, runners who normally ran once or twice a week before pandemic increased their training by 117% on average during COVID-19 pandemic, while those who previously ran up to 3 times a week, reported an increase of 55% on average (www.runrepeat.com). Thus, between government lockdowns, layoffs, furloughs, work from home mandates, school closures, and sports facility shutdowns, one of the few activities that could still be done in Italy during the various lockdowns were walking and running outdoors. This is certainly a great advantage for individual health, and we hope that such good habits will be maintained even after the pandemic, but the data obtained for LAD could also indicate that a larger release of plastic fibers from sportswear is also probable. This hypothesis, based on the effect of the increase in outdoor sports activities on the release of plastic fibers, is confirmed by a recent study that calculated a release of 347±102 microfiber/g of fabric made of 100% PEST directly to the air during an experiment performed with four volunteers who performed for 20 minutes in a clean room a series of specific movement sequences that simulated a set of normal daily activities (De Falco et al., 2020). The data from this study also demonstrated that the release of microfibers from garments to the air has the same importance as the release of microfibers to water. Therefore, it is plausible that the increase in outdoor sports activities has contributed to the increase in fibers from the synthetic sports clothing, as observed at LAD, suggesting that the rise of plastic contamination observed in the urban stretch of the Lambro River does not represent a paradox.

4.3 Final considerations

Even if we have discussed in detail only the most important results, it is still possible to identify a common behavior for all the waterbodies from the comparison between the data obtained in the two monitoring campaigns.

From a quantitative point of view, it is not possible to give a definitive response on the impact of the COVID-19 pandemic on plastic contamination, as the results are conflicting, given that in 5 watercourses we measured a decrease in the concentration of plastics, while in the others 4 waterbodies we have seen an increase (Fig. 2). Even if we focus only on the results obtained in the two most important rivers, we have observed two opposite results: a sharp drop in contamination in the Olona River, linked to an evident decrease in industrial plastic debris, mainly PMMA pellets, but a worrying increase in contamination in the Lambro River, especially for the station at the exit from Milan (Fig. 2).

If we consider the qualitative characteristics, the contamination observed during the regional lockdown is certainly simpler than in the period before the COVID-19 pandemic, as it is characterized by a smaller number of polymers, especially linked to a fragmentation of common use objects, or deriving from synthetic clothing (Figs. 6, 7). It is clear, as in the sampling carried out during the regional lockdown, the plastic debris of industrial origin almost completely disappeared in all the waterbodies, apart from a fraction of pellets of PS detected in the two sampling stations located on the Lambro River, however much lower than 2019 (Figs. 4, 6, 7). This means that one of the main effects of the COVID-19 pandemic has been the partial or permanent closure of numerous industrial activities which, from the environmental point of view, have decreased the release and therefore the contamination by plastics of primary origin in waterbodies in which they discharged directly or indirectly the wastewaters.

Lastly, our data does not seem to confirm the concerns related to a possible release of fragments or fibers from the facemasks, the massive use of which has unfortunately characterized the lives of all of us during the last two years. Indeed, they are normally made of PP, a polymer that was found at almost constant values in 2020 compared to 2019 and even much lower in some sampling stations, such as NGC, NPC, RDF and VET (Fig. 5). This result could indicate that the facemasks have been properly disposed after their use or that sufficient time has not yet passed for a massive release of PP debris by this PPE abandoned in the environment. Since the other polymers found during the 2020 monitoring campaign are not directly linked to the PPEs used during the first months of the pandemic, our data indicate that these possible sources of plastic contamination are not present in the sampled watercourses, at least for the moment.

5. CONCLUSIONS

The results obtained from the comparison of characteristics of the plastic mixtures sampled during the monitoring campaign carried out before the COVID-19 pandemic and the one performed during the regional lockdown clearly showed how the first months of the pandemic had an impact also on the plastic contamination in freshwaters. The most striking effect was certainly the change in the type of polymers present in the 7 watercourses of the metropolitan city of Milan, as there was a clear decrease, if not a zeroing, of primary plastic debris and an increase especially of fibers coming from the direct release of sportswear or due to the washing of synthetic garments. It is not possible to know whether these changes will be temporary or will become permanent, however the lesson we can draw from this particular situation is that it is evident that a change in our lifestyle and habits can also heavily influence environmental contamination. Furthermore, a problem related to the release of plastic debris from PPEs used during the pandemic does not yet appear evident, while our data suggest that the role that synthetic sportswear plays in the direct release of plastic fibers should be in-depth investigated. The fact that during the regional lockdown the massive presence of fibers also came from the washing of synthetic garments suggests that it is also necessary to deepen the topic linked to a technological improvement in the production of synthetic garments and washing machines, to allow the reduction of fibers that end up in watercourses.

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