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RECENT DEVELOPMENTS AND INNOVATIVE STRATEGIES IN ENVIRONMENTAL SCIENCES IN EUROPE

Microplastics from headwaters to tap water: occurrence and removal in a drinking water treatment plant in Barcelona Metropolitan area (Catalonia, NE Spain)

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Abstract

Nowadays, the presence of microplastics in drinking water is of concern worldwide due to potential impacts on human health. This paper has examined the presence of microplastics along the Llobregat river basin (Catalonia, Spain) and studied their behaviour and elimination along the drinking water treatment plant (DWTP). Due to different water composition, different sampling and sample preparation protocols were used to determine microplastics from river water and in the DWTP. Identification of microplastics of size range from 20 μm to 5 mm was performed by fourier-transform infrared spectroscopy (FTIR). Microplastics were detected in 5 out of 7 points along the Llobregat basin, with concentrations ranging between non-detected and 3.60 microplastics/L. In the intake of the DWTP, the mean concentration was 0.96 ± 0.46 microplastics/L (n=5), with a predominance of polyester (PES) and polypropylene (PP) and at the outlet the mean concentration was of 0.06 ± 0.04 microplastics/L with an overall removal efficiency of 93 ± 5%. Sand filtration was identified as the key stage in microplastic removal (78 ± 9%). Furthermore, the results showed that ultrafiltration/reverse osmosis (advanced treatment) is more effective for microplastic removal than ozonation/carbon filtration stage (upgraded conventional treatment). In addition, a preliminary migration test of the different materials used in the DWTP has been performed to identify potential sources of microplastics in each treatment step.

Keywords Microplastics · Drinking water · Surface water · Removal efficiency · Drinking water treatment plant

Introduction

The consumption of plastics in the European Union was of 61.8 million tonnes in 2018 and has increased progressively over the years (Plastics Europe 2019). Plastic debris spread in the aquatic environment can be slowly fragmented into tiny particles called microplastics. Microplastics are defined as a plastic particles insoluble in water, with size ranging from 1 μm to 5 mm (Frias and Nash 2019) and can be primary or secondary depending on their origin. Primary microplastics are purposefully manufactured as plastic microbeads added in cosmetics or in hygienic products (Browne 2015). Secondary microplastics are derived from weathering or fragmentation of larger plastics due to physical, chemical and biological natural processes (including abrasion or photodegradation) (Eerkes-Medrano et al. 2015) and account for the majority of microplastics in the aquatic environment (Eriksen et al. 2013). Microplastics reach freshwater systems through wastewater treatment plants (WWTPs) effluents (Murphy et al. 2016), which can contain up to 25 times more fibres than the receiving body (Talvitie et al. 2015). Small-sized microplastics and nanoplastics gain importance due to the breakdown of

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larger microplastics present in water (Enfrin et al. 2019). The most common polymers reported in rivers are polyethylene (PE) and polypropylene (PP), followed by polystyrene (PS), polyvinyl chloride (PVC) and polyethylene terephthalate (PET), while lower amounts of acrylic related compounds or polyamides (PA) are also found (Driss et al. 2018; Koelmans et al. 2019). The abundance pattern somehow follows the global polymer production (Geyer et al. 2017), and physicochemical properties such as buoyant force and polymer density play an important role in microplastic distribution in the aquatic system (Bond et al. 2018).

River water is a valuable resource to produce drinking water (Eerkes-Medrano et al. 2019). Drinking water treatment plants (DWTP) produce drinking water from raw water supplies (as rivers or groundwaters). The main purpose of the treatment is to eliminate pathogens from the water, remove undesirable chemicals, improve water quality and make it safe for human consumption. Microplastic behaviour throughout a DWTP deserves attention to ensure drinking water quality. Recently it has been reported that microplastic removal efficiency in the DWTP depends on the initial water quality in each catchment area (Pivokonsky et al. 2018; Mintenig et al. 2019; Wang et al. 2020) and the treatment applied (Novotna et al. 2019). The concentration of microplastics in drinking water is indicated in a recent review and is in general low (Eerkes-Medrano et al. 2019).

The presence of microplastics in drinking water has implications on human health (Li et al. 2018; Triebskorn et al. 2019). Today, their discharge or monitoring in water is not regulated in the European Water Framework Directive. In the case of drinking water, microplastics are also not legislated in the present European Drinking Water Directive (DWD, 98/83/EC 1998). However, it is expected that they will be included in a “watch list” in the framework of the future European DWD (European Council 2020). Other risks associated to microplastics is the potential leaching of monomers or plastic additives, such as phthalates, organophosphorus flame retardants or bisphenol A, to drinking water (Lambert et al. 2014). Many of these chemicals are considered endocrine disruptors and yet many are not regulated.

The objective of this study is to evaluate the occurrence of microplastics along the Llobregat river basin which serves as drinking water supply in the Barcelona area and study their elimination in the DWTP of St. Joan Despí. River water and water at the DWTP intake and in each treatment step was analysed to determine levels, profiles and types of microplastics and the removal rate at each treatment stage was estimated. In addition, the migration of MP from materials used in the DWTP process was evaluated. The overall goal was to assess the quality of Barcelona drinking water with regard to microplastic pollution to ensure its safety.

Materials and methods

Materials and reagents

A set of 5 stackable stainless-steel sieves of 8 cm high × 10 cm diameter and pore size of 3.5 mm, 1 mm, 300 μm, 100 μm and 20 μm (CISA, Lliçà de Vall, Spain) were used in the sampling procedure. Membrane filters of 1 μm pore 47 mm diameter polytetrafluoroethylene (PTFE) were from Savillex (Eden Prairie, MN, USA). A Vidrafoc glass filtration system (Barcelona, Spain) connected to a Vacuubrand vacuum pump (Essex, CT, USA) was used. *In situ* large volume water sampling in the DWTP was done using an immersible electro pump Hasa Inex-Palm (La Llagosta, Spain) adapted to eliminate plastic pieces and replace them with stainless-steel or PFTE.

Milli Q water was supplied by a MilliQ system (Millipore, Bedford, MA, USA). Ethanol for analysis grade was purchased from Merck (Darmstadt, Germany). Zinc chloride anhydrous was acquired from Sigma Aldrich (St. Louis, MO, USA).

Sampling of Llobregat basin

Llobregat river (NE Spain) flows through a highly anthropogenized area and at the lower course supplies raw water for drinking water production to Barcelona and its metropolitan area. It is born in Castellar de N’Hug, near the Pyrenees Mountains, a sparsely populated region, flows through central Catalonia and ends in the Mediterranean Sea near Barcelona city. It has two major tributaries: Cardener and Anoia rivers. The total river length is over 170 km, and along the basin, anthropogenic pressures increase as the river flows downstream with urbanization, industrial activities, WWTPs discharges, agriculture and historical mining. Especially past the confluence with Cardener river (very affected by potash mining activities) and Anoia river (coming from a severely industrialized area), the river shows the worst aspect. In fact, water from the Llobregat comes from more of 60 WWTP effluents (205 hm^3/year from an average river flow around 600 hm^3/year) (Marcé et al. 2012). In addition, Llobregat river exhibits the typical Mediterranean river behaviour, characterized by a high flow variability caused by seasonal rainfalls. Near the mouth, around 5 m^3/s of the surface water of the Llobregat River is uptaken into the Sant Joan Despí DWTP to produce drinking water.

Seven surface water samples were collected in 2018 along the Llobregat basin (Fig. 1), including the source (P1), after the “La Baells” dam (P2), in a midstream point situated in central Catalonia (P3) before the confluence with its two main tributaries Cardener (P4) and Anoia Rivers (P5), while P7 is the water uptake in Sant Joan Despí DWTP. Rubí creek (P6), situated in a very populated area, receives several wastewater

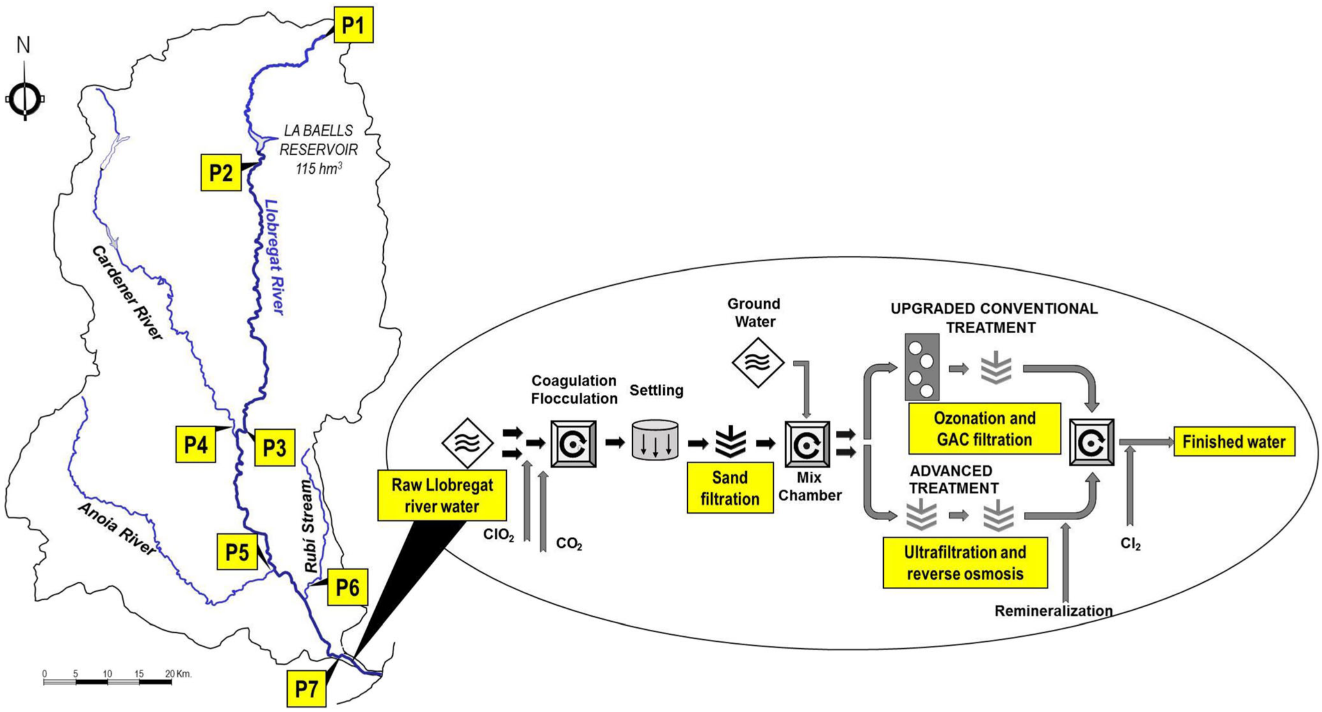


Fig. 1 Sampling location in the Llobregat river and its tributaries (Anoia and Cardener) and in the DWTP of Sant Joan Despí. In yellow, the sites that have been sampled

effluents and industrial discharges, and it is currently fully diverted due its severe pollution. Sampling of the river basin was performed once except for P7 at the DWTP inlet that was sampled 5 more times (see next section).

At each point from the Llobregat basin, 2.5 L of surface water were grab sampled and transported to the laboratory in amber bottles, with the cap protected with aluminium foil to avoid plastic contamination from the PE cap. Since Llobregat river water is characterized by a high content of particulate matter, a step of separation/flotation prior to analysis was mandatory to eliminate most of the particulate matter. River samples were first filtered along the stainless-steel sieves of 3.5 mm, 1 mm, 300 μm, 100 μm and 20 μm mesh. The sieves were rinsed with 50 mL of MilliQ water and sieve rinse containing the microplastics was collected in a 100 mL pre-cleaned glass bottle. Then, flotation was performed in a decantation funnel where the sieve rinse was dosed and 25 g of $ZnCl_2$ were added to increase the density of the solution to 1.29 g/mL, promoting plastic separation from the denser particulate matter. The supernatant liquid was collected and vacuum filtered through a 1 μm PTFE filter of 47 mm.

Sampling of the drinking water treatment plant

Sant Joan Despí DWTP, located in Catalonia (NE, Spain), supplies water to approximately 3.5 million inhabitants throughout Barcelona urban area. The potabilization scheme is shown in Fig. 1. Surface water is collected from the river, chlorine dioxide and carbon dioxide are added as initial disinfection, following by coagulation/flotation step. Afterwards, the water is driven through the sand filters. At this point, underground water from the Llobregat aquifer can be added, and then, the water is split into two parallel treatment lines. The upgraded conventional line consists in ozonation followed by Granular Activated Carbon filtering (GAC). The advanced treatment involves membrane technology (ultrafiltration followed by reverse osmosis). Water from both lines is mixed and chlorine is added to ensure the total disinfection before water is pumped into the supply network.

DWTP sampling was performed *in situ* at each treatment site and the amount of water depended on the treatment step. Samples included sand filter (50 L) and GAC filter (50 L), reverse osmosis (100 L) and treated water (100 L). Water of each stage was pumped through the immersible electro pump. Water was allowed to run before sampling for 1 minute to avoid incidental contamination. Then, the pump was connected to the full ramp of stainless-steel filtration sieves (from 3.5 mm to 20 μm) and water was filtered at a flow of 1250 mL/min. For sieves of 3.5, 1 and 0.3 mm, visual inspection was done to determine any microplastics. Sieves of 100 and 20 μm were rinsed with 50 mL of MilliQ water which was collected in a 100 mL glass bottled and thereafter filtered through a 1 μm PTFE filter of 47 mm under a vacuum system. Since the amount of particulate matter in DWTP samples and drinking water is practically insignificant, a floatation step was not necessary. Sampling along the plant was done in 5 days considering the hydraulic retention time so that within a day, raw water and samples from the 4 steps in the DWTP were collected. However, in the last 2 days water from sand filtration, GAC filtration and reverse osmosis could not be gathered. Sampling was performed during December 2018 and January 2019.

The removal efficiency was calculated as the mean of the percentage of microplastics removed each day from raw and finished water (*n*=5) and also in each treatment step.

Quantification and analysis of microplastics

Microplastic particles were detected and counted through a stereomicroscope Leica EZ4D (Wetzlar, Germany) with a magnification of 10x. Several images of the filters in each step in the DWTP are shown in Figure S1 (supporting information). These particles were classified by size and shape (fragments and fibres) considering the longest side of the particles and quantified using the software Leica Application Suite EZ 1.3.0. All particles >20 μm were collected with tweezers and a needle under a Leica DM300 stereomicroscope and placed on a 5 × 5 mm CaF_2 slide and analysed by μ-FT-IR microscope Thermo Nicolet iN10 MX/ Omnic version 7.3 equipped with an MCT array imaging detector in transmission mode (Waltham, MA, USA). Linear array detector measures two lines of 8 pixels (16 pixels at a time). Each pixel has an aperture of 25 × 25 μm. IR spectra were recorded with a resolution of 4 cm^{-1} and accumulations of 4 scans. The spectra were measured from 4000 to 800 cm^{-1}. All spectra were compared with a data base to verify the type of polymer. The concentration of microplastics was expressed as microplastics per litre (MP/L).

Migration experiments

To evaluate whether the materials used in the DWTP could release microplastic particles into the water, a preliminary migration study was performed under laboratory conditions using MilliQ water. These tests were performed using several elements used in the drinking water treatment process, specifically end of life ultrafiltration and reverse osmosis membranes and cartridges, and a section of a water supply pipe. The different materials were characterized by IR spectrum to confirm the type of polymer or combinations of polymers present in each material. To evaluate the migration of microplastics to water, the elements were individually placed in glass bottles, immersed with MilliQ water and placed in an Orbital shaker for 24 h to force the leaching of plastic polymers into the water. In the case of the water supply pipe, the tube was filled with MilliQ water to reproduce the actual conditions of contact of the water with the inner pipe. After 24 h, each material was collected and water was vacuum filtered through a PFTE membrane filters of 1 μm pore size and 47 mm diameter. Microplastics were counted and size registered, and identified using FTIR spectroscopy, as indicated previously. The microplastic results were expressed as a function of the surface area of the different elements in contact with the water during the migration tests (MP/cm^2). Given the impossibility of analysing all the particles due to their abundance in the migration tests, only a fraction of the filter was analysed, and the total concentration was then extrapolated.

Procedural blanks

To avoid external contamination, a series of measures were taken: (i) processing of samples was done in a laboratory only dedicated to analyse microplastics; (ii) glassware material was cleaned with ethanol/MilliQ water 70:30 and baked at 450°C and (iii) to discard microplastic contribution from the filtering material, stainless-steel sieves were thoroughly rinsed with 50 mL of MilliQ water:ethanol (70:30). Blank analysis of stainless-steel sieves revealed no microplastic contamination, except for 1 cellulose fibre. Additionally, blanks of washing solvents (ethanol and MilliQ water) were carried out filtering 2.5 L of each solvent through a 1 μm PTFE filter and no microplastics were identified, as the whole filtration system was done in a way that water was never in contact with the laboratory atmosphere. Finally, blanks of flotation process were performed by filtration of 2.5 L of MilliQ water along the stainless-steel sieves and then performing the flotation step as indicated before. No microplastic contribution was detected except for 2 cellulose fibres, probably from air deposition in the laboratory.

Results and discussion

Occurrence of microplastics along Llobregat basin

Microplastics detected along the Llobregat basin ranged from non-detected to 3.60 MPs/L, with a mean value of 1.60 MP/L (*n*=7). The concentration, the polymer type, the size and the shape of the microplastics are shown in Table 1. In upstream sampling points P1 and P2, no microplastics were detected as they are headwaters with little contributions from urban and industrial activities. It is relevant that P1 contained no microplastics as it is the source of the river. The absence of microplastics in P2 may be due to microplastics settling in the dam (Watkins et al. 2019). Results indicate that microplastic concentration increases downstream, with 2.00 MP/L in P3 (situated past a populated area with significant contributions of wastewater effluents) and in the two main tributaries, Cardener and Anoia rivers (P4 and P5) levels were of 3.60 and 1.20 MP/L respectively. The sampling point P7 at the DWTP inlet contained 2.40 MP/L. Rubí creek (P6) (the fully diverted due its severe pollution) showed a concentration of 2.00 MP/L.

Table 1 Number (N), size and type of microplastics along the Llobregat basin (*PES* polyester, *PS* polystyrene, *PE* polyethylene, *PP* polypropylene, *PA* polyamide, *ABS* acrylonitrile butadiene styrene)

Sampling point	Fibres		Fragments		MP/L
	N	Size (mm)	N	Size (mm)	
P1 Llobregat source	0		0		0
P2 Llobregat before dam	0		0		0
P3 Llobregat midstream	3	2.031 (PES)	2	0.133×0.468 (PE)	2.00
		0.927 (PES)		0.380×0.200 (PS)	
		1.848 (PS)			
P4 Cardener river	3	1.385 (PES)	6	1.090×0.463 (PES)	3.60
		1.199 (PES)		0.748×0.186 (PES)	
		4.452 (PP)		0.621×0.308 (PES)	
				0.448×0.516 (PE)	
				0.751×0.474 (PA)	
				0.490×0.436 (PA)	
P5 Anoia river	1	0.682 (ABS)	2	0.445×0.318 (PE)	1.20
				1.070×0.938 (PE)	
P6 Rubi creek	4	1.001 (PES)	1	0.153×0.133 (PE)	2.00
		0.623 (PES)			
		0.359 (PES)			
		1.150 (PP)			
P7 Llobregat downstream	5	0.724 (PE)	1	0.212×0.079 (ABS)	2.40
		0.327 (PP)			
		0.507 (PP)			
		0.427 (PP)			
		0.398 (PP)			
	N	**N and polymer**	**N**	**N and polymer**	
Total river	16	7 PES	12	5 PE	
		6 PP		3 PES	
		1 PS		2 PA	
		1 PE		1 PS	
		1 ABS		1 ABS	

Regarding the shape and the size, the total number of fibers was of 16 and mainly composed of PES and PP and 12 fragments mainly composed by PE (Table 1). The size of fibres was higher than the fragments. Considering both fibers and fragments, polyester (PES) was the most detected microplastic (36%) and its presence is mainly attributed to washing of synthetic clothes, followed by PP and PE (21% of each type), both widely used in packaging, labelling and construction (Geyer et al. 2017). Little amounts of PS, ABS and polyamide (PA) were found (7% of each plastic type) (Table 1).

Microplastic occurrence in river waters vary in order of magnitude, and the biggest differences are due to the technique used (Koelmans et al. 2019). Using FTIR, and preconcentrating 50 L of water, concentrations between 1.66 ± 0.64 and 8.92 ± 1.59 MPs/L were reported in surface waters of Wuhan, China, an area with more of 10 million inhabitants (Wang et al. 2017). But when using Raman spectroscopy, levels from 8.725 to 53.250 and from 7.850 to 10.950 MP/L were reported in the Pearl River in Guangzhou city, one of the most populated cities in China, with massive plastic production (Yan et al. 2019). For comparability purposes, we record the studies that use FTIR. Average values between 0.0221 and 0.1006 MP/L have been reported in Seine river and Maine rivers in Paris, sampling an average volume of 2.72 m^3 using an 80 μm plankton net. In 29 Great Lakes tributaries sampled with a 333 μm mesh neuston net, a median concentration of 0.0019 particles/L were reported (Baldwin et al. 2016). A mean of 1.2 MP/L were detected in Gallatin river watershed in USA (Barrows et al. 2018), between 0.058 and 1.265 MP/L in Antuã River in Portugal (Rodrigues et al. 2018) and 0.98 microfibers/L in the Hudson River (Miller et al. 2017). In most studies, fibres were dominant over other microplastic shapes (Horton et al. 2017a; Wang et al. 2017). However, in this bibliographic comparison, we evidenced an absence of standardized analytical methodologies that leads to a difficult - comparability of results, since there is no consensus about sampling procedures, identification and quantification methodologies nor the size analysed or the units used to report the microplastic levels, especially in drinking waters.

Microplastic behaviour along the DWTP

Microplastics were detected in all the treatment steps throughout the DWTP (Fig. 2a). Table 2 summarizes the concentrations of microplastics and the removal rate of each step throughout the DWTP. The size, the shape and the type of microplastic particles are shown in table S1 (supporting information). Raw water contained a mean of 0.96 ± 0.46 MP/L (n=5) while 0.06 ± 0.04 MP/L (n=5) were detected in finished drinking water, corresponding to an overall removal efficiency of 93 ± 5% throughout the DWTP. The elimination rates are similar to the 80-83% reported in 2 water treatment plants containing GAC filtration step, or the 70% of elimination found in the other water treatment plant without GAC filtration (Pivokonsky et al. 2018). A removal rate of 88% was reported in an advanced DWTP in the Czech Republic but only 40% in a regular DWTP (Pivokonský et al. 2020).

The removal efficiency in each treatment step was investigated (Table 2). The highest elimination rate (78 ± 9%) was observed during the first treatment stage (coagulation/sedimentation and sand filtration). The addition of aluminium salt coagulant agent produces agglutination of suspended particles and sedimentation of the coagulated matter and along with, microplastics. Afterwards, clarified water is filtered to sand layer and non-sedimented particles are eliminated. Sand filters trap microplastics by adsorption on the surface of the sand grains (Talvitie et al. 2017). A similar removal rates (up to 80%) was also observed during coagulation, sedimentation and filtration processes (Li et al. 2020). In addition, studies under laboratory conditions confirm that these steps play an essential role in microplastic removal along water treatment processes (Ma et al. 2019). The successive steps (advanced treatment and upgraded conventional) exhibited different removal efficiencies. Advanced treatment, involving filtration with membranes technology and osmosis, constitutes a total barrier to viruses, bacteria, and eliminates practically all organic and inorganic compounds present in the water and eliminated 54 ± 27% of the microplastics (n=5). In contrast, microplastic removal in the upgraded conventional treatment

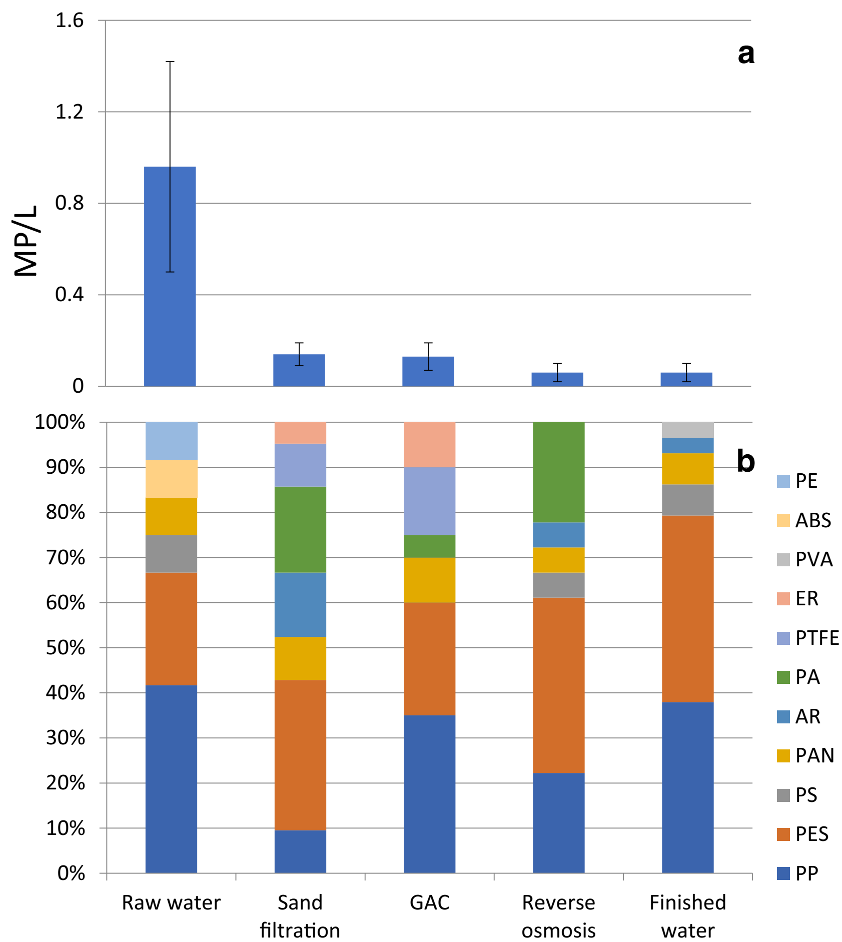


Fig. 2 **a** Concentration of microplastics (MP/L) in water along the different treatments in the DWTP and **b** patterns of the polymers detected in each treatment step (n=5). Acronyms: PE, polyethylene; ABS, acrylonitrile butadiene styrene; PVA, polyvinyl acetate; ER, epoxy resin; PTFE, polytetrafluoroethylene; PA, polyamide; AR, alkyd resin; PAN, polyacrylonitrile; PS, polystyrene; PES, polyester; PP, polypropylene

Table 2 Microplastic concentration in MP/L and removal rate in each step at the DWTP

	Raw water *n*=5	Sand filtration *n*=3	GAC filtration *n*=3	Reverse osmosis *n*=3	Finished water *n*=5
Day 1	0.80	0.10	0.06	0.07	0.11
Day 2	0.80	0.20	0.18	0.10	0.08
Day 3	0.40	0.12	0.16	0.02	0.03
Day 4	1.20	-	-	-	0.03
Day 5	1.60	-	-	-	0.04
Average concentration (mean ± Standard deviation)	0.96 ± 0.46	0.14 ± 0.05	0.13 ± 0.06	0.06 ± 0.04	0.06 ± 0.04
Microplastic removal rate (%)*	-	78 ± 9	18 ± 46	54 ± 27	93 ± 5

*Mean value calculated as the difference between the raw water and the finished water in each day

-not sampled these days

using ozonation followed by GAC filtering was 18 ± 46%, much lower than the 82.1–88.6% removal reported in a DWTP in China (Wang et al. 2020). GAC filtration retains contaminants as pharmaceuticals, drugs of abuse (Boleda et al. 2011) or pesticides (Quintana et al. 2019) but contrarily, in our study was not fully effective for microplastic elimination. It has also been suggested that the use of ozonation can increases the number of microplastics due to the breakdown caused by the water shearing force of the water flow (Horton et al. 2017b; Wang et al. 2020).

Concerning the polymer type, PP and PES were the most common microplastics along the treatment plant (Fig. 2b). This pattern is in line with that reported in previous studies (Pivokonsky et al. 2018; Wang et al. 2020). Since PP, PES, and polyacrylonitrile (PAN) were detected in Llobregat raw water and also in final treated water, it can be hypothesized that these polymers come from the river raw water. However, other microplastics found in the DWTP were not detected in the river as PTFE, epoxy resin or alkyd resin. This can be explained by the fact that Llobregat raw water contains a high amount of particulate matter and these polymers could be retained within the sediments (Horton et al. 2017a). Another reason can be that for microplastic grab sampling exhibits a high degree of uncertainly compared with the analysis of other organic pollutants homogeneously dissolved in water. In addition, because of the high turbidity of Llobregat river samples, the sampled volumes in the basin surface waters were much lower (2.5 L) than in the DWTP samples (50-100 L) and this might influence the profile of microplastics detected.

The levels of microplastics in finished water ranged from 0.03 to 0.11 MP/L, being PES and PP the main polymers detected. These levels are similar or lower that those detected in bottled water (Oßmann et al. 2018; Schymanski et al. 2018; Mason et al. 2018) or finished water (Kirstein et al. 2021). In a DWTP in Germany no particles were detected (Weber et al. 2021). The size pattern of the microplastics in the DWTP is in accordance with the previously observed trend in the river basin sampling: the fibres measured more than the fragments (Fig. 3a, Table S1). Furthermore, fibres and fragments exhibit different behaviour along the DWTP. The size pattern of the fibres was maintained relatively constant along the treatment process with a slight decrease of fibers of 20-500 µm after sand filtration but with an increase of larger fibers thereafter, and with small fibers in reverse osmosis and finished water (Fig. 3b). In contrast, a decrease in size was observed for fragments. In the raw water sampled in the intake of the treatment plant, 60% of the fragments measured between 500 and 1000 µm, 20% between 1000 and 2000 µm and 20% > 2000 µm (Fig. 3c). After sand filtration, all fragments were < 500 µm. In successive treatment steps, around 80% fragments were < 500 µm and the rest ranged in the 500-1000 µm size. In finished water, the majority of fragments were in the 200-500 µm range (Fig. 3c).

Earlier published studies reported that 1-5 µm and 5-10 µm were the predominant size of microplastics both in raw water and drinking water, and the percentage of small-size microplastics increased throughout the treatment as opposed of the percentage of larger particles (Pivokonsky et al. 2018; Wang et al. 2020). However, particle size > 1 µm is only detected using Raman spectroscopy which is a more time consuming technique and only a proportion of the filter is analysed due to cost constrictions (Käppler et al. 2016, Elert et al. 2017). In our study, the absence of microplastics below 100 µm could be due to the visual pre-sorting process. Visual sorting can be affected by the subjective criteria of the analyst, the microscopy quality and the sample matrix (Li et al. 2018). Because of this, visual sorting can lead to a significative underestimation in the smallest particle sizes.

Migration of microplastics from materials used in the DWTP

Preliminary migration experiments under controlled and forced conditions permitted to determine if microplastics could leach

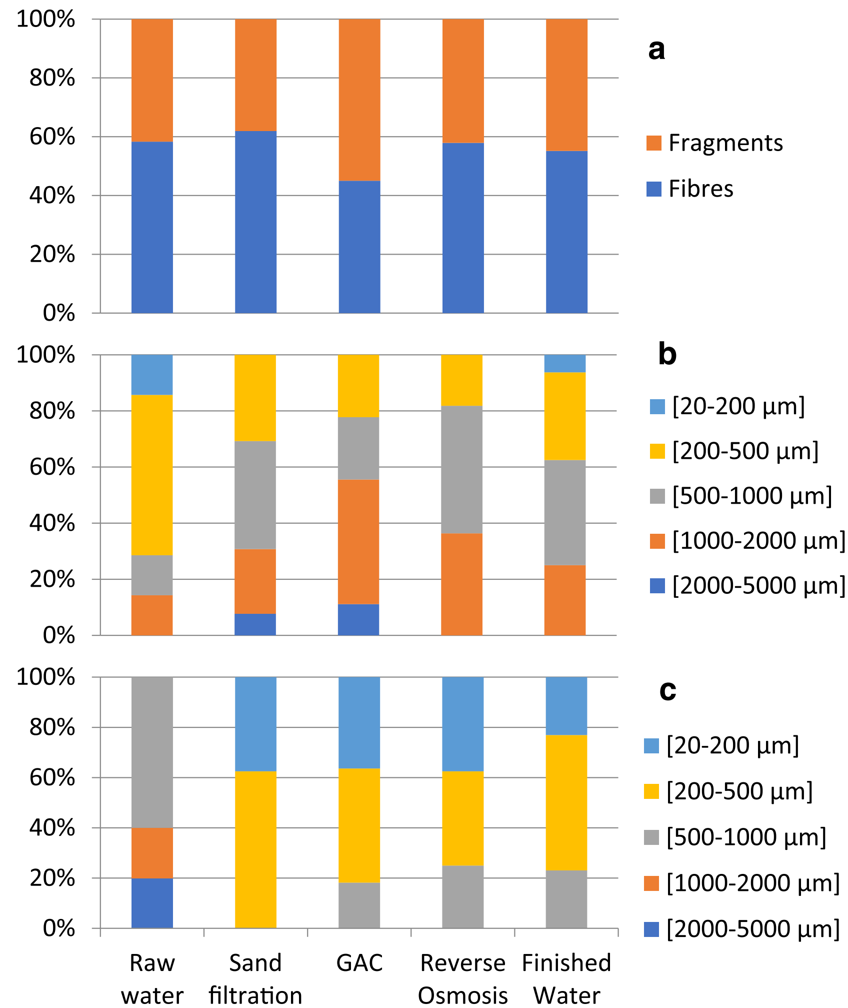


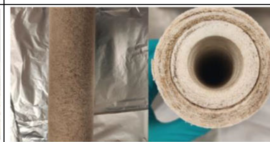
Fig. 3 **a** Percentage of fragments and fibres in the different treatment steps in the DWTP, **b** size distribution of fibres and **c** size distribution of fragments (*n*=5)

from the materials used in the DWTP. It was observed that some materials used in the plant (Table 3 to visualize the picture) can release microplastics into the water. Table 3 list the types and the sizes of each microplastic fragment or fibre detected in the migration experiments. Values between 0.006 and 0.098 microplastics/cm^2 are explained by the fact that end of live materials (worn and weathered) were used in the migration tests. One example of this is the PE water supply pipe, which released several PE fibres and fragments in the migration experiments but PE was not detected practically in any stage of the DWTP nor in the final treated water. This fact seems to indicate that in normal working conditions, the pipes are not a microplastic source, but more research is required to confirm this hypothesis. Ultrafiltration membrane exhibited a similar behaviour as these membranes are mainly made of polyvinylidene difluoride (PVDF) which leached during the migration test, although this polymer was not detected along the DWTP. On the other hand, PAN, PA and PES particles were found in the reverse osmosis membrane and in the cartridge migration tests and also in the ultrafiltration/reverse osmosis sampling point of the DWTP, but the origin of these type of particles is not clear to date because they were also previously detected in the sand filter and in the GAC filter. Therefore, these initial migration tests suggest that when materials are old, microplastics can be released to surrounding media, but this does not occur at normal DWTP working conditions. However, these are preliminary results and successive migration experiments are required to clarify if materials used during treatment can act as a potential sources of microplastics in finished water.

Conclusions

This study shows that microplastics present along the Llobregat basin and in the inlet of the DWTP are efficiently removed (93 ± 5%) and that coagulation and sand filtration are key for microplastic elimination (78 ± 9%). In addition, advanced treatment (ultrafiltration/reverse osmosis) showed better removal rates than upgraded conventional treatment (ozonation/GAC filtration). Furthermore, a decrease in the particle size of microplastic fragments has been observed throughout the drinking water treatment, but it has not been detected in the case of

Table 3 Microplastic size, shape, type and levels in the migration experiments

		Ultrafiltration membrane	Reverse osmosis cartridge	Reverse osmosis membrane	Water supply pipe
Material		PVDF	PP	PP, PET, polysulfone	PE
Image					
Dimensions		(28 cm x 0.95 mm external diameter) x 30 items	5.8 cm x 6.3 cm external diameter, with 1.7 cm thickness.	(28 cm x 10 cm) x 5 membranes	100 cm x 2.5 diameter x 0.4 cm thickness
Volume of water (L)		0.68	0.43	1.67	0.27
Area of material (cm^2)		251	243	2800	509
fibres	analysed	13	11	12	9
	total	22	130	76	14
	non-plastic	8 cellulose	8 cellulose, 1 protein	9 cellulose	8 cellulose
	plastic	4 PVDF (0.727, 0.375, 0.804, 0.981 mm) 1 PU (0.483 mm)	1 PAN/PA (0.289 mm) 1 PES (0.498 mm)	1 PAN (0.623 mm) 1 PA (0.510 mm) 1 PES (0.224 mm)	1 PE (0.419 mm)
Fragments	analysed	-	-	-	3
	total	-	-	-	3
	non-plastic	-	-	-	1 silicate
	plastic	-	-	-	1 PE (0.117x0.181 mm), 1 polysulfone (0.133x0.191 mm)
Total in whole filter	plastic	8	24	19	3
MP/cm^2		**0.032**	**0.098**	**0.006**	**0.006**

Acronyms: *PVDF* polyvinylidiene difluoride, *PU* polyurethane, *PP* polypropylene, *PAN* polyacrylonitrile, *PA* polyamide, *PES* polyester, *PET* polyethylene therephthalate, *PE* polyethylene

the fibres. The concentration of microplastics in the finished water was of 0.06 ± 0.04 MP/L, which is in the low range considering the state of art. In addition, preliminary migration tests indicate that some old and worn elements from the DWTP could be a potential source of microplastics, but no evidence of this has been found under normal working conditions. Nevertheless, future studies of microplastic migrations to the drinking water are required, in order to clarify potential sources of microplastics throughout the water drinking treatment and water supply. The knowledge and information gathered in this study are fundamental to enable future actions to control and eliminate as much as possible the presence of microplastics in finished drinking water from the Barcelona DWTP.

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Availability of data and materials All data generated in our research group and is made available.

Author contribution Joan Dalmau and Ruben Ballesteros made the sampling and experimental work, Nuria Ferrer did the FTIR analysis, Miquel Paraira, Mª Rosa Boleda and Silvia Lacorte made the sampling design, the initial study conceptualization and the identification of needs. All authors contributed to the writing.

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Declarations

Ethical approval Not applicable

Consent to participate All authors consent to participate

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