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Influence of tourism on microplastic contamination at wastewater treatment plants in the coastal municipality of Chiclana de la Frontera

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ABSTRACT

The tourism is one of the most important sources of the economy in the Bay of Cadiz. Specifically, the municipality of Chiclana de la Frontera, with a population lower than 90,000 citizens, located in the southeast of Spain. During the summer season the population duplicates leading to an increment in flow at wastewater treatment plants (WWTPs). These facilities have been reported as a source of microplastics (MPs) into marine ecosystems, therefore the aim of the present study is to investigate if the tourism affects the presence, discharge and in the receiving environment. Samples were taken at the influent and effluent of the municipal WWTPs (one located at the urban area and other located at resort area) during 2021 (including low and high season). MPs were collected and extracted from wastewater matrixes following the method recommended by the National Oceanic and Atmospheric Administration and UTS treatment to reduce organic matter and cellulose, respectively. The analysis of the samples was performed according to their abundance, shape, size, and type of polymer, along with the removal rates of MPs at WWTPs. The results showed heterogeneous MPs abundance ranging from 1246.4 to 345.7 MPs/L and 72.9 to 4.2, in the influent and effluent, respectively, increasing the presence of MPs at resort WWTP during high season. Fibers were the predominant shape within all the samples. A total of 17 polymers were identified, by ATR-FTIR, where Acrylates, PE and PA were the largest polymers found. Despite the high MPs retention performance of the WWTPs analyzed (84.1–99.3 %), a combined contribution of approximately 1.4×10^7–5.9×10^8 MPs/d to the aquatic environment was estimated. Finally, these results indicate that the increase of MPs in the wastewater at WWTP-B was related with the population increase as a consequence of summer tourism.

1. Introduction

Microplastics (MPs) are described as synthetic plastic particles or polymeric matrix with size from 1 μm to 5 mm with regular or irregular shape, of either primary or secondary manufacturing origin (Frias and Nash, 2019). Primary MPs are referred as plastics originally manufactured under 5 mm whereas, secondary MPs are generated by degradation and fragmentation of larger plastics as a consequence of physical, chemical and biological processes (Kershaw and Rochman, 2015). In 2004, Richard Thompson reported, for the first time, the presence and accumulation of small plastic fragments and fibers in the oceans arising the concern about MP pollution due to their resistance to biodegradability, potential large-scale accumulation, and ubiquity in marine ecosystem (Thompson et al., 2004). In the last decade, environmental contamination by MPs has become an issue of global concern and research purpose since these emergent micropollutants are expected to persist in the environment for centuries and have been detected worldwide, from the poles to the equator, in both terrestrial and aquatic ecosystems. The presence of MPs in marine matrixes has been widely addressed by several authors being identify in freshwater matrixes; river stream, estuarine environment, lakes, sediments, wetlands, and seawater matrixes; beach sand, seawater, water column. The introduction of MPs into the web chain has been confirmed by the presence of these pollutants in the digestive track of different aquatic animals and mammals and even in food and beverages (Huang et al., 2020; Kershaw

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Nomenclature

ATR-FTIR	Attenuated total reflection Fourier transform infrared spectroscope
CPE	chlorinate polyethylene
EVA	ethylene-vinyl acetate
GDP	gross domestic product
HDPE	high density polyethylene
LDPE	low density polyethylene
Mpart	microparticles
MPs	microplastics
NOAA	National Oceanic and Atmospheric Administration
OM	organic matter
PA	polyamide
PE	polyethylene
PEMA	poly (ethyl methacrylate)
PES	polyester
PET	polyethylene terephthalate
PI	Polymide
PMMA	poly (methyl methacrylate)
PP	polypropylene
PS	polystyrene
PTFE	polytetrafluoroethylene
PU	polyurethane
PVA	polyvinyl acetate
PVC	polyvinyl chloride
RWW	reclaimed wastewater
SDG	Sustainable development goals
SNIS	Spanish national institute of statistics
UTS	urea/thiourea/sodium hydroxide method
WPO	wet peroxide oxidation
WWTP	wastewater treatment plant

and Rochman, 2015; Truchet et al., 2023; Sewwandi et al., 2023; Shahul Hamid et al., 2018; Yabanli et al., 2019; Zhu et al., 2018).

According to Waldschläger et al. (2020), there are several pathways for MPs to enter the environment, such as surface runoff, wind and rain or effluent from wastewater treatment plants (WWTPs), the source of these micropollutants are plastic production industry activities, construction industry, sports ground, landfills, car tires, littering, cosmetics, washing effluent or loss of fishing gear. As mentioned above, WWTPs are entry paths of MPs into the environment, these facilities are designed to remove and eliminate pollutants contained in wastewater (from urban, domestic, and industrial activities) to return the treated water into the water cycle, nevertheless, wastewater treatment processes are not prepared to separate MPs from the sewage (Sun et al., 2019).

Although these facilities are not designed to treat and retire MPs, several authors have reported that conventional wastewater treatment methods can remove between 79 and 99 % of the MPs present in the water line (Nandakumar et al., 2022). Microplastics are retained and accumulate in the solid fraction of wastewater, sludge (Hamidian et al., 2021). This final product from WWTPs has become a resource as it can be used to generate bioenergy from methane and hydrogen during anaerobic digestion of the sludge, as well as used in agricultural fields as soil amendments to improve soil physical structural and nutrients contents (Tena et al., 2020; Zou et al., 2019). Furthermore, a portion of the wastewater can be further treated and cleaned to ensure its safety to be reused, this product is named reclaimed wastewater (RWW).

RWW can be used to irrigate crops, environmental enhancement (parks, rights-of-ways, and golf courses irrigation), or industrial use (to provide water for power plants, refineries, factories, and mills) (Yi et al., 2011). This sub-product follows the principles of circular economy of reduce waste and pollution, along with, achieving sustainable development goals (SDGs) number 6 focused on ensure sustainable management of water and sanitation for all, and SDG 12 dedicated to sustainable consumption and production, including the improvement in reduction and recycling of waste.

Regarding the presence of MPs in the WWTPs different unit processes have been analyzed, with heterogenous and non-comparable results due to the lack of standard sampling, quantification and identification procedures (Nandakumar et al., 2022). In a recent review publication on the characteristics of MPs in WWTPs, Hamidian et al. (2021) reported that MPs abundance in the influent vary from 1.57 to 8400 MPs/L, in studies carried out in China and Korea, respectively. Whereas in the effluent, the presence of these micropollutants decreased varying from 0.09 MPs/gal to 5800 MPs/L. These results were obtained in study performed in United States and Denmark, respectively, showing gaps in units to report the results, which increases the difficulty to compare different studies.

Another issue to addresses is the total quantity of these micropollutants released into seawater from effluents, although the removal efficiency of MPs could reach 99 % as mentioned above, however, when the daily treated volume is considered up to 10^7 the microplastics are discharged into the environment according to a previous study carried out in the province of Cadiz, while a research conducted in Illinois reported a daily mean flux of 1.38×10^6 MPs (Franco et al., 2021; McCormick et al., 2016). Therefore, the outlet act as a pathway for MP to marine ecosystems, being of interest to establish the influence of tourism, in terms of MP abundance due to the increase of water treated during high season at resort and coastal areas.

The province of Cadiz situated in southwestern Spain, has a population of 1,246,761 in 2021 according to the Spanish National Institute of Statistics (SNIS) and encompasses 45 municipalities, divided in 6 counties. The province of Cadiz has 285 km of coastline, belonging to 16 of the 45 provincial municipalities, facing the Atlantic Ocean and Mediterranean Sea. This territory is surrounded by shores and beaches, highlighting the Atlantic side of the coast, located within the called "Costa de la Luz" which extends from Tarifa and ends in the mouth of the Guadiana River in the Province of Huelva. The Costa de la Luz includes the shoreline of the municipality studied in the present study, Chiclana de la Frontera which is the sixth most populated municipality in the province of Cadiz with a population of 87,493 in 2021 (Spanish National Institute of Statistics (SNIS), 2022); this community is influenced by tourism estimating that during summer season (from July to September) up to 11.4 million visitors stayed in Chiclana de la Frontera, with a daily average of 209,065 inhabitants spending the night during the summer period. The increase of the population during the mentioned months occurred especially in the neighborhoods of La Barrosa and Novo Sancti Petri, located a few meters from the beaches of the same name. This situation leads to an increment in waste generated and wastewater to treat at the WWTP located in this part of the municipality (Adeitur, 2022).

Thus, the aim of the present study is to determine whether tourism alter the presence of MPs and increases the discharge and contamination of these micropollutants into the receiving water system at two WWTPs located in the same municipality, Chiclana de la Frontera, Cadiz. The facilities analyzed are an urban WWTP and a coastal WWTP, treating sewage from inner city and resort area, respectively. The abundance and assessment of MPs at the influent and effluent of both WWTP is researched during low and high season, to evaluate the differences on the abundance and characteristics of the microplastics (shape, size, and polymer composition) during a year time. The novelty of this study is that until now the effect of tourism on MPs pollution at WWTPs has not been widely addressed in the globe, and any research of this type has been carried out in Cadiz neither in Andalusia.

2. Materials and methods

2.1. Location and description of the WWTPs sampled

The present study was carried out during 2021 in two WWTPs located in Chiclana de la Frontera. The facilities analyzed, named in the present study as WWTP-A and WWTP-B, receive different type of wastewater; WWTP-A (36°25′38″ N; 06°09′22″ W′) is situated in the city center and treats domestic, urban and industrial wastewater from all the activities carried out in the city whereas WWTP-B (36°22′47″ N; 06°10′54″ W′) is located in a resort area which treatment volume is highly influenced by tourism. The receiving watercourses, where the effluent points are located, flow into the Caño Sancti-Petri, a marshland ecosystem within the "Bahía de Cadiz" Natural Park and is catalogued as a sensitive area in accordance with Decree 204/2005; therefore, the WWTPs analyzed include processes for eliminating nutrients from the wastewater (Decree 204/2005, n.d.).

Table 1 shows the characteristics of the WWTPs investigated in the present study and the average component of the influent at both facilities. WWTP-A and WWTP-B have two treatment lines, water line and sludge line. The water line at the facilities consisted in a pretreatment, with grease trap, grit chamber and several screens, to remove oil, grease and solids. Primary treatment with two primary clarifier, and secondary treatment; in the case of WWTP-A it consisted in simultaneous nitrification and denitrification in a bioreactor and two secondary clarifiers, whereas the secondary treatment of WWTP-B incorporates an anoxic tank followed by two clarifiers. In the sludge line, both facilities have anaerobic digestion to treat the solid fraction of the wastewater. Finally, both facilities are equipped with tertiary treatment to generate RWW with a capacity to reuse around 40 % and 1.5 % of the treated wastewater at WWTP-B and WWTP-A, respectively, which could be reclaimed for recreational use: irrigation of golf courses and for irrigation of gardens (municipal and Cemetery), nevertheless during 2021 tertiary treatment line were not operating in any of the facilities (Chiclana urban agenda 2030 (2021)).

2.2. Experimental design and sampling

Sampling was carried out periodically throughout 2021 at the WWTPs under study. A total of 48 samples were taken at two different points of the WWTPs, a) Influent, taken just after the roughing treatment, to avoid possible clogging caused by larger solids; b) Effluent, at the point immediately prior to discharge into the receiving waterway, once the water has passed through the entire wastewater treatment facility, including a refining treatment, and disinfection.

Water samples were filtered through 100 mm (4-inch) diameter stainless steel sieves of different mesh sizes (5 mm, 1 mm, 355 and 100 μm). Solids retained on the 5 mm sieve were rejected, since they are larger than microplastics. For the analysis of MPs, 5 L per sample were collected in the WWTP influent, and 50 L in the effluent.

2.3. Microplastics separation

Once the samples were filtered through the sieves, the collected particles were transferred to beakers using ultrapure water. The beakers with the samples were oven-dried at 75 °C. Once the samples were dried, the wet peroxide oxidation (WPO) method (McCormick et al., 2016) was used for the isolation of microplastics. This method consists of the addition of 20 mL of a Fe (II) 0.05 M solution and 20 mL of hydrogen peroxide (H_2O_2) at 30 % v/v to the dried sample. A magnetic stirrer was then added and covered with a watch glass to prevent external contamination. Once the reagents were added, the samples were placed in the magnetic stirring device at 75 °C and 200 rpm for 30 min. Subsequently, the samples were filtered through a 53 μm mesh sieve to remove excess reagents, collecting the samples in the same beakers. For this purpose, they were collected with as little ultrapure water as possible to correctly perform the following cellulose removal step. If in the sample collection step after sieving through 53 μm a considerable volume of ultrapure water was needed, it was dried again in the oven at 75 °C.

Samples containing cellulose were to be treated by the UTS method, which is called UTS after the acronym of its reagents (urea/thiourea/sodium hydroxide) (Egea-Corbacho et al., 2022). For this, once the samples had been sieved through 53 μm to remove the remains of the WPO reagents, 40 mL of a solution of 8 % urea, 8 % sodium hydroxide and 6.5 % thiourea (by weight) were added per 100 mg of dry sample. Once the reagents were added, the beakers with the samples were placed in the freezer at −20 °C for 40 min and then stirred until they reached room temperature. Then, again to remove reagent residues, the samples were passed through a 53 μm mesh sieve and washed 15 times with 30 mL ultrapure water. Finally, the samples were recovered in the same beakers.

For influent, the process (WPO + UTS) was repeated up to three times, in order to reduce organic matter (OM) and cellulose so that it would not interfere with the analysis of microplastics. For the effluent samples, the WPO method was performed only once, without the need to apply the UTS. Once the organic matter and cellulose were removed from the samples, the density separation step was performed. For this, 40 mL of 5 M NaCl was added and allowed to decant overnight. Finally, the samples were filtered through a polycarbonate filter with a diameter of 45 mm and 0.8 μm pore size and were dried for approximately 2 h at 40 °C.

Table 1
Characteristics of the WWTPs analyzed and influent content.

		WWTP-A	WWTP-B
Treatment capacity (m^3/year)		3,855,000	1,200,000
Population equivalent		55,000	50,000
Daily Flow (m^3/day)	Off-season	7608	4114
	Summer	7345	10,664
COD (mg O_2/L)	Off-season	679	470
	Summer	834	838
TS (mg/L)	Off-season	152	244
	Summer	300	402

2.4. Physical and chemical analysis

For the characterization of the microparticles, a physical and chemical characterization was carried out. In this way, an estimation of the MPs and identification of specific polymer types could be made.

Initial the physical characterization was performed, for this, the filters were analyzed using a Carl Zeiss Axio Imager M1m optical microscope. Considering the filter area and according to the principle of random fields, a certain number of images were taken of each sample and a particle count was performed. After quantification, the total number of microparticles (Mpart) estimate was calculated for all samples. At the same time, the Mpart were classified into five categories according to their shape: flakes, fiber, filament, fragment, and sphere, following the type of microplastics proposed by the National Oceanic and Atmospheric administration (NOAA) (Masura et al., 2015).

Subsequently, a chemical characterization was performed, which consisted of particle identification to discern whether they were polymers or not. In addition, once the plastic particles were identified, the type of specific polymer was identified. For this purpose, a Spectrum 3 Fourier Transform Infrared Spectroscope (ATR-FTIR) in attenuated total reflection mode was used. ATR-FTIR measurements were performed for the composition of the MPs, generating a spectrum for each particle analyzed. Each particle was analyzed by performing 4 scans between 4000 and 650 cm^{-1} wavelengths and a spectral resolution of 4 cm^{-1}. A total of 697 suspected particles were analyzed, of which 337 were microplastics. A similar number of particles was selected in each filter analyzed, considering that each sample had several filters due to the size separation performed. The spectra obtained were compared with the polymer spectra library and the type of MP was determined when the match rate was higher than 0.7 (Joint Research Centre, Institute for Environment and Sustainability (JRC), 2014).

2.5. Reagents and chemical products

Filters (0.8 μm polycarbonate filters PC membrane 47 mm) were purchased from Isopore™ (Darmstadt, Germany) and Petri Slide were provided by Millopore[M] (Darmstadt, Germany). The pure urea pearls (98.5 %) and extra-pure sodium chloride were provided by Scharlau (Barcelona, Spain). Iron II sulphate 7-hydrate purissimum (99.5 %), sulphuric acid (95–98 %), thiourea (98.5 %), sodium hydroxide extra pure and hydrogen peroxide (30 % v/v) were supplied by Panreac (Barcelona, Spain).

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

Monitoring contamination throughout the process is important for the analysis of MPs. Attention should be paid to implementing consistent QA/QC practices from inception through the entire study process (including during study design, sampling and collection, extraction, and analysis) to enhance the reliability and comparability of microplastic data (Brander et al., 2020). In consequence, all equipment used for sampling and laboratories were pre-washed in the same way with ultrapure water, and all materials were covered with aluminum foil.

All devices used for sampling and laboratory were pre-washed several times with distilled water and covered with aluminum foil. Sample material was transported in closed coolers that were kept insulated before, during and after sampling. Cotton clothes and gloves were worn during sampling and analysis to avoid contamination by plastic fibers.

3. Results and discussion

3.1. Abundance of microplastics and removal efficiency

Microparticles were determined for all the samples and MPs abundance was estimated after FT-IR analysis. Table 2 shows the number of microparticles per litre (Mpart/L) and microplastics per litre (MPs/L) as well as the MP removal efficiency for WWTPs A and B.

Regarding off-season samples, few differences were found between WWTPs A and B for both Mpart and MPs, as these facilities receive wastewater from similar domestic activities at this time of the year. However, a large difference was observed when comparing samples collected in summer. The amount of Mpart and MPs increased dramatically in the case of WWTP-B, which serves an area where the population is highly influenced by seasonal tourism in the summer months. This effect was not reflected in WWTP-A, where the differences in Mpart and MPs were smaller as this facility serves an area with a more constant population throughout the year. The seasonal variation on MPs at WWTPs was also addressed in a study carried out in Qingdao (China), where the occurrence of these micropollutants in summer was higher than in winter, the authors concluded that the seasonal variation was caused by the increasing presence of rayon, which was attributed to tourism activities and people lifestyle (Jiang et al., 2022).

The MPs removal efficiency was slightly lower in summer for both WWTPs. In the case of WWTP-B, despite the large difference in the amount of Mpart and MPs arriving between off-season and summer, the variation in the removal efficiency was very small (higher than 94 %), showing a robust performance of the facility despite the increase in wastewater pollution. Regarding WWTP-A, the removal efficiency ranged from 84 % to 89.9 %, this result is within the removal efficiencies reported by other authors (Table 3) where the separation of these pollutants varied from 66.1 % to 99.8 %. The differences in the efficiency of MPs removal are conditioned by the type of treatments applied (primary, secondary, and tertiary), retention time, initial load, and particle shape and density in each facility performs being difficult to provide a certain reason for the difference of microplastic removal in the present study, in addition, the physical and biological unit operations in WWTPs were not specifically designed to remove MPs. Despite the higher removal efficiency in WWTP-B, the increase in the population and volume of water received in summer has an impact that makes this facility more polluting than WWTP-A, since considering the daily volume of treated wastewater that is discharged to the environment by these plants, both release MP amounts in the same order of magnitude (5.8×10^8 MPs/d for WWTP-A and 2.4×10^8 MPs/d for WWTP-B), and although WWTP B discharges three times less daily volume treated water than A, it is more polluted.

The number of MPs released daily by WWTP-B off-season is an order of magnitude lower (1.4×10^7 MPs/d), which is a remarkable difference in wastewater pollution. At WWTP-A, this daily amount of MPs is almost constant throughout the year (5.9×10^8 MPs/d off-season and 5.8×10^8 MPs/d in summer). These results are within the estimation of MPs released by WWTPs in previous reports, where the daily flux of MPs varied from 4.3×10^4 MPs/day to 42.5×10^9 MPs/d (Jiang et al., 2022; Sun et al., 2019). Table 3 shows a summary of previous research articles addressing the presence of MPs in wastewater; however, it is not possible to compare these results as the volume of wastewater treated, the characteristics of the sewage, the difference on the treatment lines in each facility, and the lack of standardized methods to collect, separate and quantify MPs samples.

Table 2
Microparticles per litre (Mpart/L), microplastics per litre (MPs/L) and microplastic removal efficiency (%) for all the samples analyzed.

		WWTP-A		
		Mpart/L	MPs/L	% MP removal efficiency
Off-season	Influent	1034	557.5	89.9
	Effluent	143	56.4	
Summer	Influent	437	345.7	84.1
	Effluent	78	55	

		WWTP-B		
		Mpart/L	MPs/L	% MP removal efficiency
Off-season	Influent	927.5	580.2	99.3
	Effluent	92.5	4.2	
Summer	Influent	1966	1246.4	94.2
	Effluent	159.4	72.9	

3.2. Occurrence and distribution of MPs

3.2.1. Distribution by particle morphology

In terms of physical and chemical characteristics (size and shape) of the MPs, all the studies read agree that fibers are the most abundant shape followed by fragments, this distribution is explained by the arrival of washing effluent it was reported that a single garment releases up to 0.1 mg of fiber per gram of textile washed, which generates a large load of fibers to the wastewater (Hernandez et al., 2017). Fig. 1 shows the relative abundance of the four morphological categories into which the microparticles were classified: flake, filament, fragment, and fiber, for both WWTPs. It is noteworthy, the absence of sphere microplastics in the present study, this issue may be explained by the ban or restriction on the use of these microparticles in cosmetics and personal use products as exfoliants or shower gel in some European counties (Vuola et al., 2019).

Fibers were the most abundant microparticles in all the samples analyzed, ranging from 40.7 % to 67.2 % of the total counted microparticles. This is a common characteristic of microparticles in wastewater samples and has been previously described in numerous studies (Talvitie et al., 2015; Lares et al., 2018; Franco et al., 2021). These fibers

Table 3
Summary of the results reported in previous studies at WWTPs to determine the presence of MPs in wastewater.

WWTP location	MP abundance (MP/L)	Removal of MPs from WWTPs	Main shape	Predominant polymers	Reference
Qingdao, China	Influent: – Effluent: 12.3–67.3	–	Fibers	Rayon, PET, CPE	Jiang et al., 2022
Mikkeli, Finland	Influent: 57.6 ± 12.4 Effluent: 1 ± 0.4	98.3 %	Fibers (82 %)	PES, PE, PA	Lares et al., 2018
Sydney, Australia	Influent: 55–98 Effluent: 0.18–0.91	98.2–99.8 %	Fibers (49–88 %)	PET, PE, PP	Ziajahromi et al., 2021
Wuhan, China	Influent: 23.3–66.1 Effluent: 80.5–30.3	66.1–62.7 %	Fibers (59.7–73.2 %)	PVC, PA, PE	Tang et al., 2020
Medina Sidonia, Spain	Influent: 92.7–793.5 Effluent: 10.9–47.6	85.1–98.5 %	Fibers (29.2–94.2 %)	PET, PS, PP, PE	Martín-García et al., 2023
Karmiel, Israel	Influent: 65–130 Effluent: 1.97–7.3	95.8–97.0 %	Fibers (74–91 %)	PI, PE, PES	Ben-David et al., 2021
Chiclana WWTPA, Spain	Influent: 345.7–557.3 Effluent: 55–56.4	84.1–89.9 %	Fibers (40.7–67.2 %)	Acrylate, PE.	Present study
Chiclana WWTPB, Spain	Influent: 580.2–1246.4 Effluent: 4.2–72.9	94.2–99-3 %	Fibers (41.1–57.9 %)	Acrylate, PE, PP.	Present study

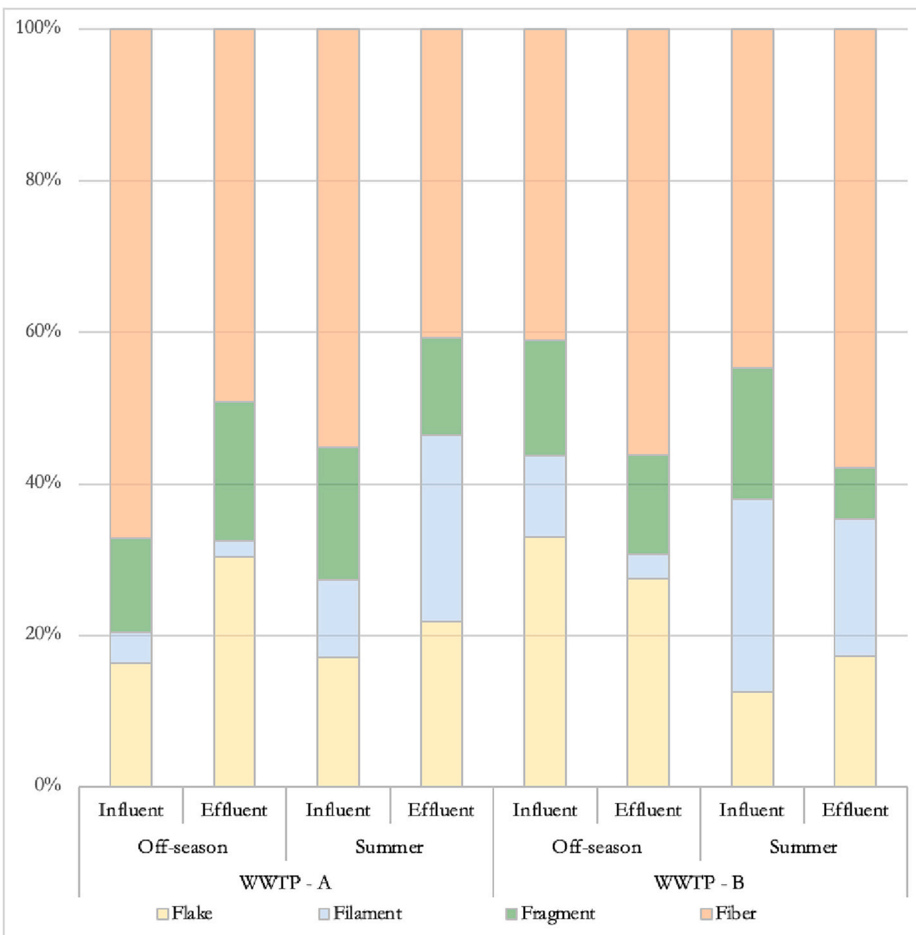

Fig. 1. Relative abundance of microparticle morphologies in summer and off-season for both influent and effluent samples at WWTPs A and B.

originate from household laundry activities. Due to their low width/length ratio and light weight, it is usual to find these microparticles in effluent samples as they are hardly removed in conventional treatment units such as degreasing or decantation (Mason et al., 2016; Ben-David et al., 2021). Fragments abundance was very similar, regardless of the WWTP or sample type, ranging from 12.4 % and 18.4 % in most of the samples analyzed. The behavior of other morphologies such as flakes and filaments was more irregular between seasons and WWTPs, and there did not seem to be a clear pattern describing how these types of microparticles vary depending on the sample studied.

At WWTP-A, the relative abundance of fibers decreased in effluent samples relative to influent in both off-season and summer due to an increase in other morphologies such as flakes and filaments. In WWTP-B, fiber abundance increased in effluent samples relative to influent samples, a behavior that is consistent with the results described by other authors (Martín-García et al., 2023; Michielssen et al., 2016) and more common than that found at WWTP-A.

Although some similarities can be found between both WWTPs, such as the higher proportion of filaments in the summer months or the slight variation of fragments, it is difficult to find patterns that show differences or similarities between these facilities, since the time of the year or the location seems to have little influence on the morphological characteristics of microparticles in wastewater.

3.2.2. Size distribution

Fig. 2 shows the relative abundance of the three size categories into which the microparticles were classified, for both WWTPs. Microparticles ranging from 100 to 355 μm were found to be the most abundant size in most of the samples, both for influent and effluent samples. The larger size category (1000–5000 μm) ranged from 8.2 to 38.3 % of the total number of microparticles, but these percentages tend to decrease in effluent samples, where are a higher relative abundance of smaller microparticle sizes (355–1000 μm and 100–355 μm) which can sum up to 91.8 % of the total counted microparticles in the sample. This can be understood considering the physical and chemical processes the microparticles are subjected to throughout the wastewater treatment. Some of these microparticles are broken into smaller pieces that are more difficult to remove and scape from the treatment units, so its presence is more abundant in effluent samples. It has been indicated that microparticles ranging from 125 to 355 μm are the most abundant in wastewater (Mason et al., 2016), which is in consonance with previous study carried out in the province of Cadiz (Franco et al., 2020). However, size distribution has not been widely analyzed during the wastewater procedure at these facilities, but the abundance of smaller MPs increases in the effluent due to the removal of larger microplastics in the first stages of wastewater treatment (Nandakumar et al., 2022; Martín-García et al., 2022).

3.3. Determination of polymer types

After physical characterization, the microparticles were analyzed using ATR-FTIR in order to identify their chemical composition and to distinguish plastic and non-plastic materials. At WWTP-A, 53.9 % (off-season) and 79.1 % (summer) of the microparticles analyzed in influent were identified as MPs, while in effluent, MPs accounted for 39.1 % (off-season) and 70.5 % (summer) of the microparticles identified. At WWTP-B, MPs represented 62.5 % (off-season) and 63.4 % (summer) of the total microparticles in influent samples, and 4.5 % (off-season) and 45.8 % (summer) in effluent samples.

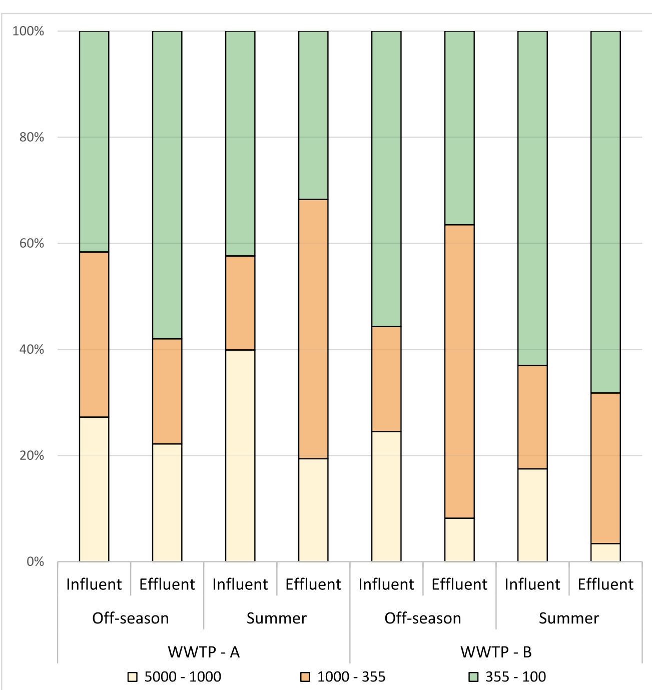

Fig. 2. Relative abundance of microparticle sizes in summer and off-season for both influent and effluent samples at WWTPs A and B.

As shown in Section 3.1 (Table 2) there is a higher proportion of MPs in the effluent samples in summer at both WWTPs, but this does not imply a reduction in the removal efficiency of these pollutants from the wastewater, but it is due to the higher arrival of MPs at the inlet, which means that higher amounts of MPs are discharged in the summer months even though the removal efficiency is almost constant throughout the year.

Regarding plastic polymers, up to 17 and 25 different polymers were identified at WWTPs A and B, respectively. Some of the most abundant polymers identified were PA (2.9–18.4 %), PE (11.5–45.9 %), HDPE (3.25–17.9 %), PP (3–35.3 %), PS (3.6–12.1 %), polymers of the acrylate family (PEMA, PMMA, 20.6–75.8 %) and other minor polymers that were grouped in the category “Others” (EVA, LDPE, PES, PET, PU, PTFE, PVA or PVC, 0.75–26.6 %). Some of the most abundant polymers found, such as PE or PP, coincide with the most demanded and consumed plastics in domestic environments, as other authors have reported in previous studies (Tang et al., 2020; Ziajahromi et al., 2021). Fig. 3 shows the relative abundance of the polymers identified for all the samples analyzed.

At WWTP-A, few differences were detected between off-season and summer samples, except for the detection of PP in summer, while at WWTP-B, PA was not detected in summer. This small variation may indicate different uses of plastics throughout the year.

In the case of acrylates, their proportion increases in summer at both WWTPs, which can be an indicator of a variation in population activities that makes these polymers more abundant in the wastewater, acrylates are widely used in multiple applications due to their hardness, transparency, flexibility and toughness, being used in adhesives, cosmetics or textiles as polymeric fibers (Kema Ajekwene, 2020), the extensive use of these family of polymers could explain their presence in the present study. The large MP heterogeneity in the samples demonstrates a wide variety of activities and plastic demand, which shows the importance of the influence of the population activities and habits on the presence and abundance of different polymer types. An approach to this fact can provide valuable information about the impact that MPs from wastewater can have on the environment and living beings.

3.4. Summer effect in MPs contamination

The importance of the tourism sector is reflected in the economic and employment contribution generated by this sector in southern Spain. According to regional government, tourism and travel sector contribute for 25 % to gross domestic product (GDP) in Andalusia (Iamkovaia, 2021), during summer 2021 this employment sector generated a direct input of 827 million euros in Chiclana de La Frontera, which represented approximately a 31 % of the GDP of the municipality. However, when indirect and induced profits are taken into account the tourist sector comprise 60 % of the total GDP in Chiclana de la Frontera, with an income amount of 1621.7 million euros during summer 2021 (Adeitur, 2022). As shown in Table 2 the abundance of MPs at WWTP-B in summer triples the concentration of these micropollutants during the rest of the year, 1246,4 MPs/L and 345,7 MPs/L, respectively; when comparing both facilities, WWTP emplaced in the resort area (WWTP-B) duplicates the presence of MPs respect to WWTP-A. One of the origins of the increment of MPs in the wastewater during the summer at WWTP-B could be the increase of laundry of textiles during the summer season, as a consequence of high concentration of tourism and the more frequent and larger volume of textile consumption at hotels and resorts by the daily use, disposal and clean of towels, sheets, tablecloths or napkins; in this line, a study conducted in Guilin, a tourist city in China, linked the increase of MPs in the wastewater to the degradation of larger plastics used in the tourist sector to transport, accommodation, and catering, which were suggested as potential sources of MPs (Zhang et al., 2021).

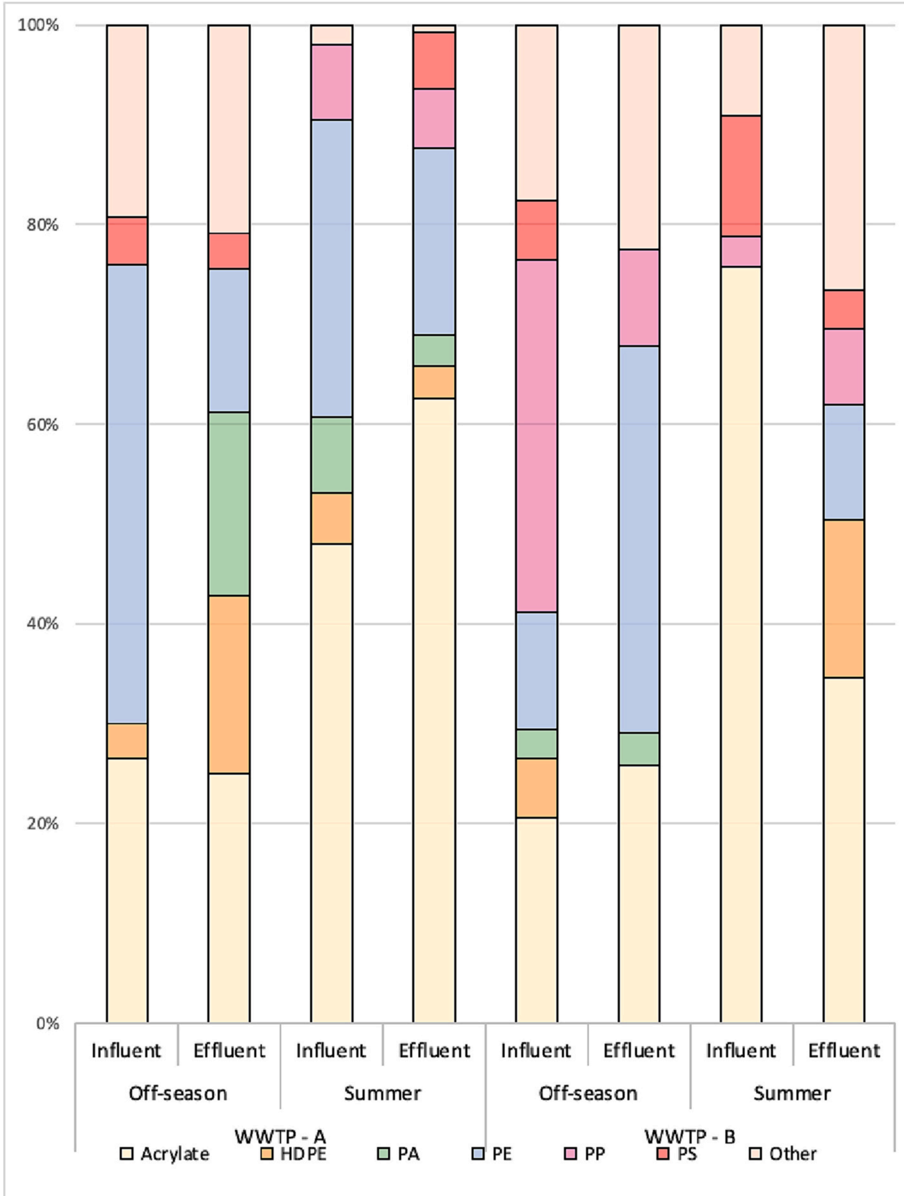

Fig. 3. Relative abundance of the plastic polymer types identified with ATR-FTIR for all the samples analyzed.

Regarding the type of MPs.

The increase in the presence of MPs during summer at WWTP-B is in line with the fluctuation on waste generation. In Chiclana de la Frontera during 2021 a total of 65,000 TM of waste were generated, collected, and treated. Table 4 shows the solid waste generated by touristic and local population, considering the municipal solid waste stream and difference in the input of waste by local inhabitants and tourism, it is noticed that during summer season the waste generated by visitors is higher than waste by local population (Adeitur, 2022). Furthermore, this data demonstrates the marked seasonality of tourism in the area, and the increase in general pollution (including waste and microplastic release) during summer season, especially in the resort area (Chiclana urban agenda 2030 (2021)).

Table 4
Solid waste generated in tons during each season in 2021. Data: Adeitur, 2022

	Local population waste	Tourism waste
Winter	9740	3994
Spring	9849	6777
Summer	9957	10,509
Autumn	9920	4515

Regarding the characteristics of the wastewater at the influents of the WWTPs analyzed (Table 1), the daily flow of wastewater arriving at WWTP–A did not present significant variance during the year varying from 7608 to 7345 m3/day, whereas at the other facility an average of 10,664 m3 arrive daily during summer months in contrast to the 4114 m3/day received during the rest of the year; this might be explained by several reason; a) the increase of the population during summer season especially in La Barrosa and Caño de Sancti Petri area, where WWTP-B is located, b) the variation in the water consumption during holidays as a result on the changes in the habits and uses of water by consumers; this assumption is in line with the use and wastewater generation of water by seasons reported by the European Environmental Agency (EAA) (2019), in summer 3023 hm^3 are utilized in the continent whereas in the other seasons the consumption average is 2500 hm^3.

COD has been used as a measurement of pollutants in wastewater, as shown in Table 1, WWTP-B duplicates COD concentration in summer

(838 mg O_2/L) in comparison to the average values reported the rest of the year (470 mg O_2/L), these demonstrate the increase in the contamination of the wastewater as a result of the population growth generated by tourism in the resort area, whereas COD at WWTP-A, suffered a slight increase from 679 mg O_2/L during off-season to 834 mg O_2/L.

4. Conclusions

This study assessed the effect of seasonality tourism in MPs pollution at two WWTPs located in Chiclana de la Frontera, these facilities are affected differently by tourism and recreational summer activities. The results showed that wastewater arriving to the WWTP situated in the urban zone (WWTP-A) did not presented differences in terms of daily flow, COD, SS, however, WWTP-B located in the resort area was highly influenced by seasonality of tourism increasing the pollution of the wastewater arriving to the facility during summer period respect to the rest of the year. Regarding the presence of MPs, between 1246.4 MPs/L and 345.7 MPs/L were found in the influent, whereas in the effluent the abundance of presence of plastic varied from 72.9 MPs/L to 4.2 MPs/L, at the facilities analyzed. WWTP-A did not present significant differences in the abundance of MPs throughout the year, while WWTP-B doubled the presence of MPs in the influent during the summer in comparison with the rest of the year at WWTP-B, and in the effluent the quantity of MPs was 17 times higher in the summer samples respect to the concentration of MPs during off-season. The shapes and sizes of the MPs indicated that the fibers and fragments were the most abundant, probably from the textile laundry release and fragmentation of large plastics, respectively; as to size distribution, the smaller microparticles fraction analyzed was the most abundant (355–100 μm) in the samples. Regarding the presence of different type of polymer, a total of 25 were found in the wastewater, showing the heterogeneity of the polymer composition. The most abundant polymers in the present study were Acrylates, PE and PA. Finally, the removal efficiency at the WWTPs overcome 84 % in all the cases showing a correct accomplishment to separate MPs from wastewater. However, when considering the daily volume treated the estimated release of MPs at WWTP-A does not vary significantly during the year, 5.8×10^8 MPs/d during the summer and 5.9×10^8 MPs/d the rest of the year, whereas WWTP-B increases the MPs discharge into the environment in an order of magnitude from 1.4×10^7 MPs/d off season and 5.8×10^8 MPs/d in summer, demonstrating that the increase of population derived from tourism in summer period effect negatively the environment and increasing the release of these micropollutants into the marine ecosystems. Authors propose to continue studying the enhancement in MPs pollution as a consequence of seasonality of tourism; encouraging to investigate the fluctuation MPs at other facilities influenced by summer vacation and the variation of MPs in sludge, as these micropollutants are accumulating in the solid fraction.

CRediT authorship contribution statement

Ana Amelia Franco: Conceptualization, Methodology, Investigation and Writing Original Draft.

Diana Iglesias Arroyo: Investigation.

Ágata Egea-Corbacho: Conceptualization and Writing Original Draft.

Ana Pilar Martín-García: Term, Investigation and Writing Original Draft.

José María Quiroga: Founding, Term, Conceptualization, Review & Editing.

Maria Dolores Coello: Founding, Term, Conceptualization, Review & Editing.

Declaration of competing interest

The authors confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

Data availability

Data will be made available on request.

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