Journal Pre-proof

Temporal variation of the microplastic concentration in a stream that receives discharge from wastewater treatment plants

S. Montecinos, S. Tognana, W. Salgueiro, C. Frosinini

PII: S0269-7491(23)01778-5

DOI: https://doi.org/10.1016/j.envpol.2023.122776

Reference: ENPO 122776

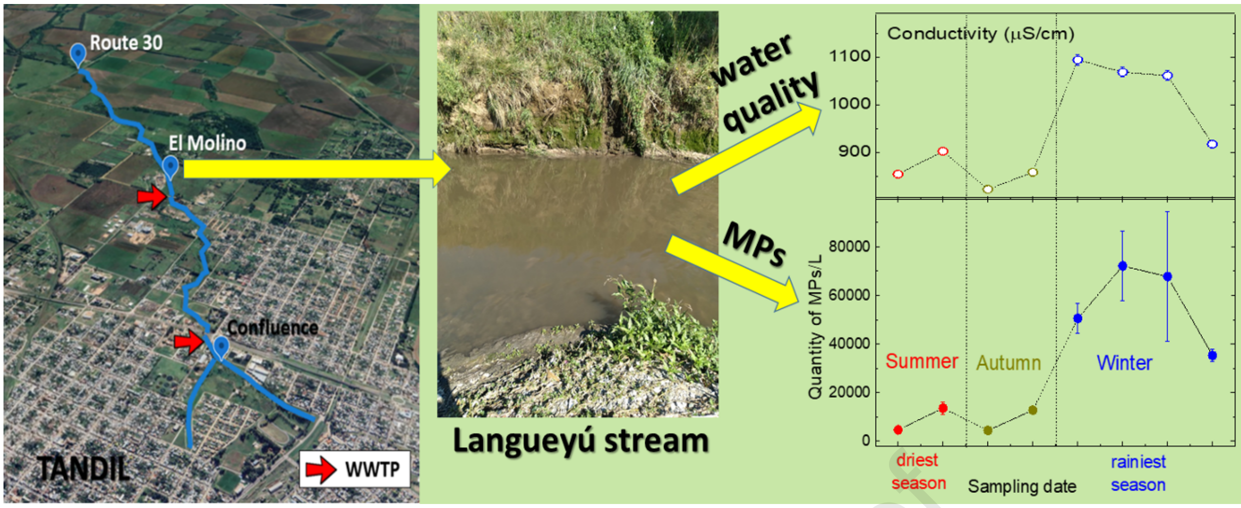
To appear in: *Environmental Pollution*

Received Date: 30 June 2023

Revised Date: 16 October 2023

Accepted Date: 17 October 2023

Please cite this article as: Montecinos, S., Tognana, S., Salgueiro, W., Frosinini, C., Temporal variation of the microplastic concentration in a stream that receives discharge from wastewater treatment plants, *Environmental Pollution* (2023), doi: https://doi.org/10.1016/j.envpol.2023.122776.


Route 30
El Molino
Confluence
TANDIL
WWTP
Langueyú stream
water quality
MPs
Conductivity (µS/cm)
1100
1000
900
80000
60000
40000
20000
0
Quantity of MPs/L
Summer
Autumn
Winter
driest season
Sampling date
rainiest season

Temporal variation of the microplastic concentration in a stream that receives discharge from wastewater treatment plants

S. Montecinos[1, 2, 3*], S. Tognana[1, 2, 4], W. Salgueiro[1, 2, 4], C. Frosinini[1, 2, 4]

1 Universidad Nacional del Centro de la Provincia de Buenos Aires (UNCPBA), Facultad de Cs. Exactas, IFIMAT, Tandil 7000, Buenos Aires, Argentina.

2 CIFICEN, UNCPBA-CICPBA-CONICET, Tandil 7000, Buenos Aires, Argentina.

3 CONICET, Buenos Aires 1425, Argentina.

4 Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, La Plata 1900, Buenos Aires, Argentina.

[*] Corresponding author: S. Montecinos. Universidad Nacional del Centro de la Provincia de Buenos Aires (UNCPBA), Facultad de Cs. Exactas, IFIMAT, CIFICEN, Argentina. Tel: +54(0)249 4385670; Fax: +54(0)249 4385679. E-mail address: dmonteci@exa.unicen.edu.ar

Abstract

The temporal variation of the microplastic concentration was studied in the Langueyú stream, which is located in the department of Tandil, in the southeast of the Buenos Aires province in Argentina. This stream receives discharge from the wastewater treatment plants from a medium-sized city. A quantitative analysis of the microplastic concentration was carried out in different samplings, corresponding to different seasons. The study focused on the most contaminated point, located after the discharge of effluents from plants. Higher concentrations of MPs were found in winter (dry season), having approximately 6 times the concentrations found in summer and autumn (wet seasons). However, these differences would not be a direct consequence of the amount precipitation, but rather would be associated with a seasonal variation of human activities, mainly with respect to the type of clothing used in the cold season. The microfibers correspond to around 60 to 90% of microplastics found. The discharge from the plants causes changes in the parameters of the stream water, such as high electrical conductivity values, and also provide metallic contaminants such as Ca, Zn, and in smaller amounts Pb, Fe, Ni and Cu, which were found adhered to the microplastics and remain in the stream water in high quantities 3 km after the study point. The microplastic concentration presents a linear empirical correlation with the conductivity, and it was found that conductivity measurements would serve as an indicator of the microplastic concentration in the system under study.

Keywords: Plastic pollution; Effluent discharge; Watercourse; Seasonality; Water quality.

1.- Introduction

Plastics have become essential materials in the daily life of people and for different industrial, technological, and health applications. In the last decades, world plastics production has had an increasing trend and has reached 390.7 million tons in 2021, with packaging and construction being the largest markets for plastics (Plastics Europe, 2022). In recent years, the inadequate disposal of post-consumer plastic waste has generated an emerging environmental problem, mainly due to plastic debris with sizes smaller than 5 mm, which are commonly called microplastics (MPs) (Boucher and Friot, 2017; Thompson, 2007). MPs have been found all over the world and in different environments, especially in aquatic environments. In recent years, their presence in oceans, seas, estuaries, lakes, and rivers, among others, has been studied (Forero-López et al., 2021a; Islam 2022; Li et al., 2018; Wang and Wang, 2018).

Due to their small size, MPs can be easily ingested by aquatic species, causing damage to their health (Amini-Birami et al. 2023; Arias et al., 2019; Kalčíková, 2023), and can also be transferred reaching higher trophic levels and humans (Ji et al., 2023). Furthermore, MPs can act as a source and sink for toxic contaminants, such as metals, organic pollutants, and chemical additives, because they have the ability to absorb or adsorb and release the contaminants into the organisms (Ahmed et al., 2023; Forero López et al., 2021b; Godoy et al., 2019; Yu et al., 2019). This property increases the risk of toxic effects on organisms when MPs are ingested.

Rivers and streams can accumulate large amounts of MPs and transport them into the seas and oceans (Hoellein et al., 2019; Lebreton et al., 2017; Schmidt et al., 2017; Tanaka et al., 2022). The amounts of MPs reported in different rivers and streams differ greatly from less than one to several million items per m^3 (Li et al., 2018; Montecinos et al., 2021; Mora-Teddy and Matthaei, 2020; Schmidt et al., 2017). The MP concentration depends on the population density near the water course or upstream, the proximity to urban centers, the characteristics of the water body, the type of waste management used, and the quantification methodology, among other factors (Eerkes-Medrano et al., 2015; Li et al., 2018; Nihei et al., 2020; Stock et al., 2019). The presence of wastewater treatment plants (WWTPs) that discharge their effluents into the watercourse is one of the main sources of MPs (Li et al., 2018; Mintenig et al., 2017; Montecinos et al., 2021; Montecinos et al., 2022; Sun et al., 2019). Microfibers have been found to be the most important type of MPs present in rivers and streams, which are mainly released during mechanical drying of clothes and textiles in household washing machines (Belzagui et al., 2020; De Falco et al., 2019; Maja et al., 2023; Montecinos et al., 2021).

The Langueyú stream is located in the southeast of the Buenos Aires province, in the Argentine Pampas. It receives discharge of WWTPs effluents from the city of Tandil. In previous studies, the contribution of urban sewage discharges to MP contamination in the Langueyú stream was studied (Montecinos et al., 2021; Montecinos et al., 2022). 97% of the total MPs came from WWTPs effluents, while the rest came from storm drains and discharge of tributaries. The most polluted area corresponded to a point after the discharge of the plants, with a concentration of around 72000 MPs/L. At this point, around 70% of the MPs corresponded mainly to polyethylene microfibers, with a mean length of around 300 µm. At the most polluted point, the presence of copper in the MPs present in the stream was analyzed and confirmed using the LIBS technique (Tognana et al., 2022). The retention of copper by MPs that have been in contact with stream water and the influence of organic matter were also studied. The Langueyú stream has a low flow and receives a high discharge of MPs, mainly from the WWTPs that process wastewater from a medium-sized city. These characteristics make the study of this stream of great importance as a comparative case with respect to others with similar characteristics. However, the values of MP concentration found at the same point but from different samplings and dates, and reported in different works, are very different and cannot be compared between them (Montecinos et al., 2021; Montecinos et al., 2022). These variations in the MP concentration could be associated with seasonality, climatic conditions, and the behavior of the WWTPs. There are very few studies on the temporal distribution of MPs in rivers. Wu et al. (Wu et al., 2020) studied the spatial-temporal distribution of MPs in the surface water and sediments along the main stream of the Maozhou river in China, while Xia et al. (Xia et al., 2020) investigated the relationship between precipitation and MP concentration in the surface water of Donghu lake in China. In Argentina, Pazos et al. (Pazos et al., 2021) studied temporal patterns in the abundance of MPs on the coast of the Río de la Plata estuary.

The aim of this work is to study the temporal variation of the MP concentration in a stream that receives discharge from WWTPs from a medium-sized city, especially in the most contaminated point, located after the discharge of effluents from the WWTPs. A quantitative analysis of the MP concentration was carried out in different samplings, corresponding to different seasons. The MP concentration found in each sampling was analyzed with respect to the measured physical parameters of the stream water, and climatic conditions. The presence of metallic contaminants in the MPs extracted from the stream water was also analyzed by X-Ray fluorescence measurements.

2.- Materials and methods

2.1. Study sites

This study was carried out in the Langueyú stream, which is located in the department of Tandil (37° 04´ S; 59° 08´O) in the southeast of the Buenos Aires province in Argentina. The city of Tandil has a population of around 150162 inhabitants (INDEC, 2022) and occupies an approximate area of 50 km^2. The Langueyú stream receives discharge of effluents from two WWTPs that process wastewater from the city of Tandil. In a previous work in the Langueyú stream basin, it was reported that the point of highest MP concentration corresponded to the one located after the discharge of WWTPs in a zone located in the El Molino area (Montecinos et al., 2022). The present study was carried out in the El Molino area (Fig. 1), after the discharge of WWTPs. In order to study the presence, main sources and transport of metallic contaminants in the MPs present at the point under study, water samples from a point before (Confluence) and after the El Molino area (intersection with Route 30) were additionally analyzed. Confluence corresponds to the point where the Langueyú stream forms, from the confluence of Del Fuerte and Blanco streams and before the discharge of the WWTPs. The intersection of the Langueyú stream with Route 30 is about 3 km further on from the El Molino area and no significant sources of MPs would be expected between the two points.

FIGURE 1

At the main extraction point, located in the El Molino area, the Langueyú stream has a width that varies between 5 and 7.7 m, with a minimum width in the sampling of August 10, 2021, and a maximum width in the sampling of February 10, 2022. On the other hand, the maximum depth was located mostly at the midpoint of the stream and varies between 0.3 and 0.6 m, with a minimum depth in the samplings of March 29, 2021, and August 10, 2021, and a maximum depth for June 30, 2023. The speed of the stream water reached its highest value at its midpoint, with maximum values around 0.6 m/s. From the depth profiles measured in each sampling, and using the speed values measured at different points of the stream cross section, the stream flow was estimated for each sampling. The values obtained for each sampling are shown in Fig. 2. Flow values between 0.7 and 1.0 m^3/s were estimated, with a minimum for August 27, 2021 and March 29, 2021, and a maximum for June 30, 2023. It is important to point out that the profile of the stream undergoes continuous changes due to the cleaning tasks that are carried out in the stream. Flow values for three sampling dates at the Confluence point are also indicated in Fig. 2 to analyze the contribution of WWTPs discharge to the stream flow. Of the water flow measured at El Molino, 30% comes from tributaries, while 70% comes from plant effluents for the February 2022 sampling. For the August 2021 sampling, these percentages change to 25 and 75%, respectively, while it changes to 15 and 85% for the June 2023 sampling.

FIGURE 2

2.2. MPs sampling and analysis

The samplings were carried out on different days corresponding to different seasons in the city of Tandil: February 18, 2021 and February 10, 2022 (summer); March 29, 2021 and June 2, 2021 (autumn); August 10 and August 27, 2021, September 20, 2021, September 15, 2022 and June 30, 2023 (winter). The specific sampling dates were selected based on the mean values of historical temperature and precipitation in the city of Tandil (Fig. S1). The water temperature was measured with a TES 1300 thermometer with an accuracy of 0.1°C.

Three water samples were collected from the stream surface (up to 10 cm depth) in each sampling using 1 L volume glass bottles. Samples were extracted at points approximately equidistant from both shorelines. The physical properties of the water samples were measured using an A1 TDS&EC portable meter for electrical conductivity (EC) and a Hach portable pH meter for pH. The density of the samples was estimated by determining the volume of the extracted water and weighing it with a Systel balance with a precision of 1 g.

For the quantification of the MPs, each water sample was filtered through a 1.5 mm mesh steel filter, and particles with sizes smaller than 1.5 mm were filtered through a 45 µm mesh Besmak steel filter. Particles with sizes between 45 µm and 1.5 mm were removed from the filter using distilled water and kept. To remove organic matter, samples were subjected to an oxidative digestion process using a 30% hydrogen peroxide solution for 2 h at 50°C. Then, samples were washed using a 45 µm steel filter and extracted from the filter with distilled water. Drops of the concentrated solution, consisting of MPs and distilled water, were placed on glass slides using a 50 µL micropipette. At least three drops of each sampling were visually analyzed under an Arcane XSZ-100BNT trinocular microscope. Then, using the ImageJ 1.52p software, MPs were quantified, and their morphology was characterized, considering two types: microfibers and microparticles. Microfibers are MPs that have one dimension much longer than the other, while microparticles are those where all dimensions are of the same order of magnitude. Only the MPs with the largest dimension greater than 100 µm were considered for quantification, because those with sizes between 45 and 100 µm present a degree of uncertainty regarding whether they are MPs or not. Mean values of each sampling were calculated, and differences were compared using a one-way analysis of variance (ANOVA), where differences were considered significant for $p < 0.05$.

X-Ray fluorescence measurements were performed on a Rigaku R-XAS Looper using an Amptek Si detector. The energy of the incident beam was that corresponding to the K_α emission line of Mo (17.48 keV), and a Si monochromator was used. The size of the entrance slit to the sample chamber was optimized according to its dimensions, being approximately 10 x 0.4 mm^2. Measurements were made with the detector forming an angle of 90° with the incident radiation, and the sample was placed with one of its faces at 45° between the incident beam and the detector. Energy calibration was performed using the characteristic fluorescence lines of various metallic patterns. For X-Ray fluorescence measurements of the MPs, concentrated samples were filtered through a membrane of 22 µm pore size, and the retained content was measured.

2.3. Quality assurance and quality control

To avoid the contamination of the samples during their processing, several measures were taken. The use of plastic instruments was avoided as much as possible, and glass beakers and metallic equipment were used for handling the samples. All laboratory instruments were washed with distilled water and dried before use. Cotton laboratory coats and latex gloves were worn during the manipulation of the samples. During processing, samples were placed into a clean glass chamber to keep them covered and protected from airborne MPs. In order to validate the quality of the method, the experimental recovery percentage was measured using different filings from different commercial polymers, with a particle length in the range of 200 to 1000 µm. The particles were added to distilled water in a proportion around 0.01 %P/V and the recovery experiment was carried out following the same methodology of the stream samples. The obtained recovery rates were of 89.8% for polypropylene, 94.6% for acrylic and 96.8% for polyamide.

Three blanks of distilled water were subjected to the same methodology of the stream samples. A mean of 232 ± 49 MPs/L was obtained, with 93% of microfibers. The mean length of the microfibers was 667 µm.

3.- Results

3.1. Meteorological information

The monthly maximum (T_{max}) and minimum (T_{min}) temperatures corresponding to the historical average values of the period 1991-2022 in the city of Tandil are shown in Fig. 3(a) (SMN, 2023). In the month of February (summer season), T_{max} is 27°C, while T_{min} is 13°C. In autumn, T_{max} decreases to 25°C and T_{min} to 11°C in March, while in June T_{max} reaches 13°C and T_{min} decreases to 2°C. Subsequently, in winter, temperatures increase slightly, reaching 17°C and 4°C of T_{max} and T_{min}, respectively, in September. The historical average values of accumulated monthly precipitation corresponding to the period 1991-2020 in the city of Tandil are shown in Fig. 3(b) (SMN, 2023). The rainiest season corresponds to summer, while the driest season is winter. The accumulated precipitation 2, 5 and 10 days before each sampling date is also shown in Fig. 3(b) (Meteotandil, 2023). If the accumulated precipitation 10 days before each sampling is considered, a behavior similar to the monthly history is observed. However, a very low level of precipitation is observed the two days prior to each sampling, with values less than 4 mm.

The highest levels of precipitation were observed in the samplings carried out in the months of February and March, reaching 50 mm during the 10 days prior to the extractions. On the other hand, in June, August, and September, the precipitation levels were less than around 10 mm, even considering the accumulated precipitation during the 10 days prior to each sampling. The differences in the precipitation levels in the previous days were reflected in a higher flow measured at the Confluence in February 2022 compared to the flow measured at the same point in August 2021 and June 2023 (Fig. 2).

FIGURE 3

3.2. Samplings results

The water temperature (T_w) was measured during each sampling, and the values obtained are shown in Fig. 3(a). It is observed that T_w exhibits similar values with respect to T_{max} in June, August, and September, while it presents lower values for the months of February and March. The pH and EC values of the water samples extracted from the stream are shown in Fig. 4. pH is in the range of 6.7 to 8.8, with the highest values for the February 2021 and March 2021 samplings, while the lowest value is for June 2023. EC is in the range of 820 to 1094 μS/cm, with the highest values for the June 2023 and August 2021 samplings, while the lowest value occurs in March 2021. For comparison, a sample of distilled water has a conductivity of 10 μS/cm. The density of the water samples was measured and almost no variation was found between the different samplings, with values in the range of 0.99 to 1.00 g/ml.

FIGURE 4

MPs found on each sampling date were quantified and the results are shown in Fig. 5(a). The data of water blank samples are also included. In the samplings carried out in summer and autumn, MP concentrations lower than 14000 MPs/L were obtained. However, in samplings carried out in winter, the concentrations exceed 35000 MPs/L, even reaching 70000 MPs/L in the sampling of August 10, 2021. According to the results of the one-way ANOVA test, the MP concentration values of the August samplings were significantly different compared to the other samplings ($p<0.05$). However, the other samplings cannot be considered as significantly different.

The MP concentration found in the water blank sample corresponds to about 5% of the minimum concentration (March 29, 2021) and about 0.3% of the maximum concentration (August 10, 2021). The percentage of microfibers found in each sampling is shown in Fig. 5(b). Percentages around 60% of microfibers were found in samplings of February 2022 and March 2021. This value increases to around 75% of microfibers in samplings of February 2021, June 2021, and August 2021, while it reaches a percentage of 90% of microfibers in September 2022. It can be observed that the water blank sample contains 93% of microfibers.

FIGURE 5

3.3. X-Ray fluorescence measurements

As seen in Fig. 5(a), the highest MP concentration was measured on August 10, 2021. The presence of metallic contaminants contained in the MPs found in this sampling was analyzed by X-Ray fluorescence. A spectrum obtained from the MPs present in the study site (El Molino) is shown in Fig. 6. MP samples were also obtained at a point prior to the discharge of the WWTPs (Confluence), and at a later point located approximately 3 km from El Molino (intersection with Route 30). To the best of our knowledge, there would be no significant sources of contamination between El Molino and the intersection with Route 30. The spectra of the MPs found at the Confluence and at the intersection with Route 30 are also presented in Fig. 6. The presence of different metallic contaminants was detected in all the MPs samples, but in different proportions (Fig. 6(a)). Small amounts of Fe, Ni and Cu were found at the Confluence (Fig. 6(b)). After the discharge of effluents from the treatment plants, in El Molino, higher levels of these contaminants and high levels of Ca and Zn were measured (Fig. 6(b) and (c)). A small amount of Pb was also detected in El Molino. Those higher level of contaminants will be associated with effluents from the WWTPs. At a later point, the intersection with Route 30, the levels of metallic contaminants decreased, around 50% of Ca, Zn and Cu, and around 20% of Fe, while Ni and Pb remained at low levels. In a previous work, the presence of Cu was found in the MPs extracted from the stream water in the El Molino zone (Tognana et al., 2022).

FIGURE 6

4.- Discussion

4.1. Temporal variation of the MP concentration

As was observed in Fig. 3(b), the precipitation levels for February and March samplings were higher than those of June, August, and September. These levels of precipitation slightly influence the stream flow in the Confluence, but no significant influence is observed on the stream flow in El Molino (Fig. 2). On the other hand, higher MP concentrations were measured in the June 30, August and September samplings (winter), with considerably lower levels in the February, March, and June 2 samplings (summer and autumn) (Fig. 5(a)). The MP concentrations in winter are approximately 6 times the concentrations found in summer and autumn.

With the aim of becoming independent of the differences in the stream flow of each sampling, the MP flow expressed in MPs/s is shown in Fig. 7. A behavior similar to that of the MP concentration in MPs/L is observed, indicating that the slight differences in the flow of the stream would not influence the behavior found in the MP flow.

FIGURE 7

Wu et al. (Wu et al., 2020) studied the temporal variation of MPs in water samples from a river in China intensively surrounded by industries and found that the MP concentration in dry season is relatively higher than those found in the wet season, following a behavior similar to the results found in this study. Xia et al. (Xia et al., 2020) studied the relationship between rainfall and MP concentration in the surface waters of Donghu lake in China and found a close relationship between rainfall and MP abundance. On the other hand, Pazos et al. (Pazos et al., 2021) studied temporal patterns in the abundance of MPs on the coast of the Río de la Plata estuary and found that the wind from the northwest direction was associated with a lower abundance of MPs in the water. However, they also found that the abundance of MPs in the water was not correlated with the precipitations or other hydrological variables on the sampling date or in the 10 days prior to the date. According to the different studies reported and the results found in this work on the dependence of the MP abundance on non-anthropogenic factors, such as precipitations or the intensity and direction of the wind, it can be concluded that this relationship strongly depends on the characteristics of the aquatic system studied and the sources of MPs contamination. In the system studied, the main source of MPs is the effluents from the WWTPs.

Although it was found that the MP concentration is higher in the dry season, this would not be a direct consequence of the amount of precipitation, since flow variations are much less important than the variation of the MP concentration between the different dates. Therefore, no great influence of dilution is expected. On the other hand, nor clear relationship between accumulated precipitation in the days prior to each sampling date and MP concentration was found. In this way, it would be expected that the differences in the MP concentration are mainly due to temporal variations in human activities. As was indicated above, the main sources of MPs in the Langueyú stream are effluents from the WWTPs. The quality of the water discharged by the WWTPs also presents variations between the different seasons, being remarkable the increase in conductivity. In the months of August and September there is a greater amount of MPs and a lower water quality. This phenomenon may be associated with a seasonal variation of human or industrial activities. The influence of human's activities on seasonal variations of the MP concentration have been reported in some regions of the world (Jiang et al., 2022). However, this type of variation depends on the economic activities, habits or type of clothing, among other aspects of the region. In this case, a greater number of microfibers in the discharge from the WWTPs could be associated with a greater number of microfibers released in the laundry, considering that the months of June 30, August and September correspond to the cold season, where heavier clothes are used. Several studies have determined the emission of MPs from household laundry, finding values of up to 18000000 microfibers per 6 kg of washed clothing (De Falco et al., 2019; Galvão et al., 2020; Hazlehurst et al., 2023). A correlation was observed between the weight of synthetics fibers in each wash and the microfibers released (Galvão et al., 2020). However, the influence of the type of fabric on the amount of MPs released is complex (Hazlehurst et al., 2023).

4.2. Relationship between water quality parameters and MP concentration

In the water samples obtained from the stream in June 30, August and September (winter), when high MP concentrations were obtained, a high EC and a slightly lower pH are observed (Fig. 4). These changes in the parameters of the stream water would be related to the discharge from the WWTPs. In a previous study (Montecinos et al., 2022), EC was studied at different points of the Langueyú stream basin, finding that EC increases around 60% at the point after the discharge of the WWTPs (El Molino) with respect to a point before the discharge of the plants (the Confluence). According to a visual inspection carried out, no water contributions were observed between the Confluence and El Molino, which would indicate that the main contribution of contaminants between both points would correspond to the discharge of effluents from the plants.

In accordance with the National Law N° 26221, sewage effluents before reaching the receiving body must have pH values ranging between 6.5 and 8 (National Law, 2007). Therefore, a decrease in the pH of the stream water samples would suggest an increase in the amount of effluent from the plant. This result agrees with that shown in Fig. 2, where it is observed that in the June 30, 2023 sampling, the water flow at the El Molino point has a higher percentage of effluents from the WWTPs. This greater contribution of effluents would produce a greater contribution of dissolved ions from the water treated in the plants, which would also explain the increase in EC. In a previous work where the presence of MPs in the Langueyú stream basin was analyzed, an increase in the concentrations of different ions was reported due to the discharge of WWTPs (Montecinos et al., 2022). In that study, it was found that the highest EC value was after discharge from the WWTPs, which is also the point of highest concentration of MPs. Based on these results, it could be expected that a temporal variation in the activity of the plant produces a greater contamination by MPs and a deterioration of the water quality of the stream.

As was observed in Fig. 4 and 5(a), the concentration of MPs exhibits a similar behavior with respect to the EC of the samples. To analyze this dependence, the MP concentration was plotted as a function of EC (Fig. 8) and a linear empirical correlation (R^2 = 0.8912) is observed between both parameters. These results would indicate that EC measurements would serve as an indicator of the MP concentration in the system under study, that is, in a system where the contribution of both, MPs and contaminants, comes mainly from the effluents of the WWTPs. The use of EC as an indicator is of great importance to be able to have a first estimate on the MPs levels in this system. However, the use of EC measurements as an indicator of the MPs level should be considered with caution in other types of systems.

The conductivity of water has been used as a tracer to study longitudinal patterns of MP concentration in the North Shore Channel (NSC), which connects Michigan lake with the Chicago river in USA (Hoellein et al., 2017) and in an experimental stream (Hoellein et al., 2019). They used the ratio of MPs to conductivity to analyze deposition or resuspension.

FIGURE 8

As was observed in Fig. 6, WWTPs effluents also provide metallic contaminants such as Ca, Zn, Pb, Fe, Ni and Cu, which were adhered to the MPs. These metallic contaminants are transported by the MPs and remain in the stream water in high quantities 3 km after the study point. This fact is worrying, since they can affect the ecosystem present in the entire course of the stream.

5.- Conclusions

The temporal variation of the MP concentration was studied in the Langueyú stream, which is located in the department of Tandil, in the southeast of the Buenos Aires province in Argentina. This stream receives discharge from WWTPs from a medium-sized city. The study focused on the most contaminated point, located in the El Molino area after the discharge of effluents from the WWTPs. A quantitative analysis of the MP concentration was carried out in different samplings, corresponding to different seasons. From this study the following conclusions are obtained:

- Higher concentrations of MPs were found in winter, having approximately 6 times the concentrations found in summer and autumn. Although it was found that the MP concentration is higher in the dry season, this would not be a direct consequence of the amount of precipitation.

- In the studied system, the main source of MPs is the effluents from the WWTPs, with around 60 to 90% of microfibers, which come mainly from clothing microfibers released during household laundry. The variations of the MP concentration between the different seasons would be associated with a seasonal variation of human activities, mainly with respect to the type of clothing used in the cold season.

- Discharge from the WWTPs causes changes in the parameters of the stream water, such as high EC and slightly lower pH values. The MP concentration presents a linear empirical correlation with the EC, and it was found that EC measurements would serve as an indicator of the MP concentration in the system under study.

- The WWTP effluents also provide metallic contaminants such as Ca, Zn, Pb, Fe, Ni and Cu, which were found adhered to the MPs and remain in the stream water in high quantities 3 km after the study point.

Acknowledgements

This work was partially supported by Agencia Nacional de Promoción Científica y Técnica, Argentina (PICT-2021-GRF-TI-00100); Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina (CONICET); Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, Argentina (CICPBA); and SECAT (UNCPBA), Argentina.

References

Ahmed, A.S.S., Billah, M.M., Ali, M.M., Bhuiyan, M.K.A., Guo, L., Mohinuzzaman, M., Hossain, M.B., Rahman, M.S., Islam, M.S., Yan, M., Cai, W., 2023. Microplastics in aquatic environments: A comprehensive review of toxicity, removal, and remediation strategies. Sci. Total Environ. 876, 162414. https://doi.org/10.1016/j.scitotenv.2023.162414.

Amini-Birami, F., Keshavarzi, B., Esmaeili, H.R., Moore, F., Busquets, R., Saemi-Komsari, M., Zarei, M., Zarandian, A., 2023. Microplastics in aquatic species of Anzali wetland: An important freshwater biodiversity hotspot in Iran. Environ. Pollut. 330, 121762. https://doi.org/10.1016/j.envpol.2023.121762.

Arias, A.H., Ronda, A.C., Oliva, A.L., Marcovecchio, J.E., 2019. Evidence of microplastic ingestión by fish from the Bahía Blanca estuary in Argentina, South America. Bull. Environ. Contam. Toxicol. 102, 750-756. https://doi.org/10.1007/s00128-019-02604-2.

Belzagui, F., Gutiérrez-Bouzán, C., Álvarez-Sánchez, A., Vilaseca, M., 2020. Textile microfibers reaching aquatic environments: A new estimation approach. Environ. Pollut. 265, 114889. https://doi.org/10.1016/j.envpol.2020.114889.

Boucher, J., Friot, D., 2017. Primary microplastics in the oceans: A global evaluation of sources, IUCN, Gland, Switzerland, https://doi.org/10.2305/IUCN.CH.2017.01.en.

De Falco, F., Di Pace, E., Cocca, M., Avella, M., 2019. The contribution of washing processes of synthetic clothes to microplastic pollution. Sci. Rep. 9, 6633. https://doi.org/10.1038/s41598-019-43023-x.

Eerkes-Medrano, D., Thompson, R.C., Aldrige, D.C., 2015. Microplastics in freshwater systems: A review of the emerging threats, identification of knowledge gaps and prioritization of research needs. Water Res. 75, 63-82. https://doi.org/10.1016/j.watres.2015.02.012.

Forero-López, A.D., Rimondino, G.N., Truchet, D.M., Colombo, C.V., Buzzi, N.S., Malanca, F.E., Spetter, C.V., Fernández-Severini, M.D., 2021a. Occurrence, distribution, and characterization of suspended microplastics in a highly impacted estuarine wetland in Argentina. Sci. Total Environ. 785, 147141. https://doi.org/10.1016/j.scitotenv.2021.147141.

Forero López, A.D., Truchet, D.M., Rimondino, G.N., Maisano, L., Spetter, C.V., Buzzi, N.S., Nazzarro, M.S., Malanca, F.E., Furlong, O., Fernández Severini, M.D., 2021b. Microplastics and suspended particles in a strongly impacted coastal environment: Composition, abundance, surface texture, and interaction with metal ions. Sci. Total Environ. 754, 142413. https://doi.org/10.1016/j.scitotenv.2020.142413.

Galvão, A., Aleixo, M., De Pablo, H., Lopes, C., Raimundo, J., 2020. Microplastics in wastewater: microfiber emissions from common household laundry. Environ. Sci. Pollut. Res. 27, 26643–26649. https://doi.org/10.1007/s11356-020-08765-6.

Godoy, V., Blázquez, G., Calero, M., Quesada, L., Martín-Lara, M.A., 2019. The potential of microplastics as carriers of metals. Environ. Pollut. 255, 113363. https://doi.org/10.1016/j.scitotenv.2021.147141.

Hazlehurst, A., Tiffin, L., Sumner, M., Taylor, M., 2023. Quantification of microfibre release from textiles during domestic laundering. Environ. Sci. Pollut. Res. 30, 43932–43949. https://doi.org/10.1007/s11356-023-25246-8.

Hoellein, T.J., McCormick, A.R., Hittie, J., London, M.G., Scott, J.W., Kelly, J.J., 2017. Longitudinal patterns of microplastic concentration and bacterial assemblages in surface and benthic habitats of an urban river. Freshw. Sci. 36(3), 491–507. https://doi.org/10.1086/693012.

Hoellein, T.J., Shogren, A.J., Tank, J.L., Risteca, P., Kelly, J.J., 2019. Microplastic deposition velocity in streams follow patterns for naturally occurring allochthonous particles. Sci. Rep. 9, 3740. https://doi.org/10.1038/s41598-019-40126-3.

INDEC, 2022. National Population and Housing Census 2022. https://www.indec.gob.ar. Last access 24 May 2023.

Islam, T., Li, Y., Rob, M.M., Cheng, H., 2022. Microplastic pollution in Bangladesh: Research and management needs. Environ. Pollut. 308, 119697. https://doi.org/10.1016/j.envpol.2022.119697.

Ji, J., Wu, X., Li, X., Zhu, Y., 2023. Effects of microplastics in aquatic environments on inflammatory bowel disease. Environ. Res. 229, 115974. https://doi.org/10.1016/j.envres.2023.115974.

Jiang, F., Wang, M., Ding, J., Cao, W., Sun, C., 2022. Occurrence and Seasonal Variation of Microplastics in the Effluent from Wastewater Treatment Plants in Qingdao, China. J. Mar. Sci. Eng. 10, 58. https://doi.org/10.3390/jmse10010058.

Kalčíková, G., 2023. Beyond ingestion: Adhesion of microplastics to aquatic organisms. Aquat. Toxicol. 258, 106480. https://doi.org/10.1016/j.aquatox.2023.106480.

Lebreton, L.C.-M., Greer, S.D., Borrero, J.C., 2012. Numerical modelling of floating debris in the world's oceans. Mar. Pollut. Bull. 64, 653-661. https://doi.org/10.1016/j.marpolbul.2011.10.027.

Li, J., Liu, H., Chen, J.P., 2018. Microplastics in freshwater systems: A review on occurrence, environmental effects, and methods for microplastics detection. Water Res. 137, 362-374. https://doi.org/10.1016/j.watres.2017.12.056.

Maja, V., Sanja, V., Teresa, R.-S., Jasmina, A., Zoran, C., Jelena, R., Aaleksandra, T., 2023. Improving of an easy, effective and low-cost method for isolation of microplastic fibers collected in drying machines filters. Sci. Total Environ. 892, 164549. https://doi.org/10.1016/j.scitotenv.2023.164549.

Meteotandil, 2023. Tandil automatic weather station 2023. http://meteotandil.com.ar/index.htm. Last accessed 23 June 2023.

Mintenig, S.M., Int-Veen, I., Löder, M.G.J., Primpke, S., Gerdts, G., 2017. Identification of microplastic in effluents of waste water treatment plants using focal plane array-based micro-Fourier-transform infrared imaging. Water Res. 108, 365–372. https://doi.org/10.1016/j.watres.2016.11.015.

Montecinos, S., Tognana, S., Pereyra, M., Silva, L., Tomba, J.P., 2021. Study of a stream in Argentina with a high concentration of microplastics: preliminary analysis of the methodology. Sci. Total Environ. 760, 143390. https://doi.org/10.1016/j.scitotenv.2020.143390.

Montecinos, S., Gil, M., Tognana, S., Salgueiro, W., Amalvy, J., 2022. Distribution of microplastics in a stream that receives discharge from wastewater treatment plants. Environ. Pollut. 314, 120299. https://doi.org/10.1016/j.envpol.2022.120299.

Mora-Teddy, A.K., Matthaei, C.D., 2020. Microplastic pollution in urban streams across New Zealand: concentrations, composition and implications. N. Z. J. Mar. Freshwater Res. 54(2), 233-250. https://doi.org/10.1080/00288330.2019.1703015.

National Law N° 26211, Sewerage regulations, 2007. Honorable Congress of the Argentine Nation. https://www.argentina.gob.ar/normativa/nacional/ley-26221-125875/actualización. Last access 2 June 2023.

Nihei, Y., Yoshida, T., Kataoka, T., Ogata, R., 2020. High-Resolution mapping of Japanese microplastic and macroplastic emissions from the land into the sea. Water 12, 951. https://doi.org/10.3390/w12040951.

Pazos, R.S., Amalvy, J., Cochero, J., Pecile, A., Gómez, N., 2021. Temporal patterns in the abundance, type and composition of microplastics on the coast of the Río de la Plata estuary. Mar. Pollut. Bull. 168, 112382. https://doi.org/10.1016/j.marpolbul.2021.112382.

Plastics Europe: Plastics-the Fact 2022, 2022. https://plasticseurope.org/knowledge-hub/plastics-the-facts-2022/. Last accessed 6 June 2023.

Schmidt, C., Krauth, T., Wagner, S., 2017. Export of plastic debris by rivers into the sea. Environ. Sci. Technol. 51, 12246-12253. https://doi.org/10.1021/acs.est.7b02368.

SMN, 2023. National Meteorological Service of Argentina 2023. https://www.smn.gob.ar/estadisticas. Last accessed 23 June 2023.

Stock, F., Kochleus, C., Bänsch-Baltruschat, B., Brennholt, N., Reifferscheid, G., 2019. Sampling techniques and preparation methods for microplastic analyses in the aquatic environment-A review. Trends Anal. Chem. 113, 84–92. https://doi.org/10.1016/j.trac.2019.01.014.

Sun, J., Dai, X., Wang, Q., van Loosdrecht, M.C.M., Ni, B.-J., 2019. Microplastics in wastewater treatment plants: detection, occurrence and removal. Water Res. 152, 21–37. https://doi.org/10.1016/j.watres.2018.12.050.

Tanaka, M., Kataoka, T., Nihei, Y., 2022. Variance and precision of microplastic sampling in urban rivers. Environ. Pollut. 310, 119811. https://doi.org/10.1016/j.envpol.2022.119811.

Thompson, R.C., 2006. Plastic debris in the marine environment: consequences and solutions, in: Krause, J.C., von Nordheim, H., Bräger, S. (Eds.), Marine Nature Conservation in Europe Proceedings of the Symposium Held in Stralsund, Bundesamt für Naturschutz (BfN), Bonn, Germany, Vol. 193, 107-115.

Tognana, S., D'Angelo, C., Montecinos, S., Pereyra, M., Salgueiro, W., 2022. Laser induced breakdown spectroscopy (LIBS) as a technique to detect copper in plastic and microplastic waste. Chemosphere 303, 135168. https://doi.org/10.1016/j.chemosphere.2022.135168.

Wang, W., Wang, J., 2018. Investigation of microplastics in aquatic environments: An overview of the methods used, from field sampling to laboratory analysis. Trends Anal. Chem. 108, 195-202. https://doi.org/10.1016/j.trac.2018.08.026.

Wu, P., Tang, Y., Dang, M., Wang, S., Jin, H., Liu, Y., Jing, H., Zheng, C., Yi, S., Cai, Z., 2020. Spatial-temporal distribution of microplastics in surface water and sediments of Maozhou River within Guangdong-Hong Kong-Macao Greater Bay Area. Sci. Total Environ. 717 (2020) 135187. https://doi.org/10.1016/j.scitotenv.2019.135187.

Xia, W., Rao, Q., Deng, X., Chen, J., Xie, P., 2020. Rainfall is a significant environmental factor of microplastic pollution in inland waters. Sci. Total Environ. 732, 139065. https://doi.org/10.1016/j.scitotenv.2020.139065.

Yu, F., Yang, Ch., Zhu, Z., Bai, X., Ma, J., 2019. Adsorption behavior of organic pollutants and metal son micro/nanoplastics in the aquatic environment. Sci. Total Environ. 694, 133643. https://doi.org/10.1016/j.scitotenv.2019.133643.

FIGURES

Fig. 1. Map of the Langueyú stream from its source to the intersection with Route 30, located in Tandil, Buenos Aires province, Argentina. WWTPs discharges and extraction points are shown. Images were adapted from Google Earth, June 2022, https://earth.google.com.

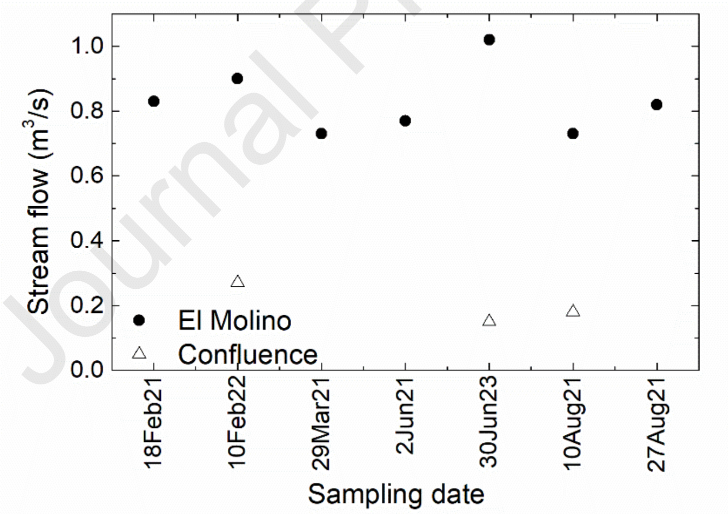


Fig. 2. Stream flow for each sampling date.

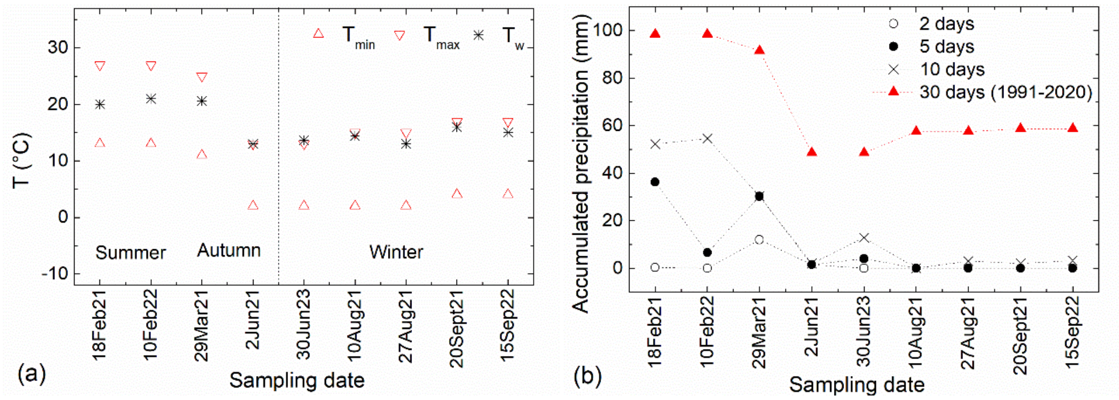


Fig. 3. (a) Historical monthly temperatures, T_{max} and T_{min}, and the measured temperature of the stream water for each sampling date, T_w. (b) Historical accumulated monthly precipitation (30 days (1991-2020)) and accumulated precipitation 2, 5 and 10 days before each sampling date.

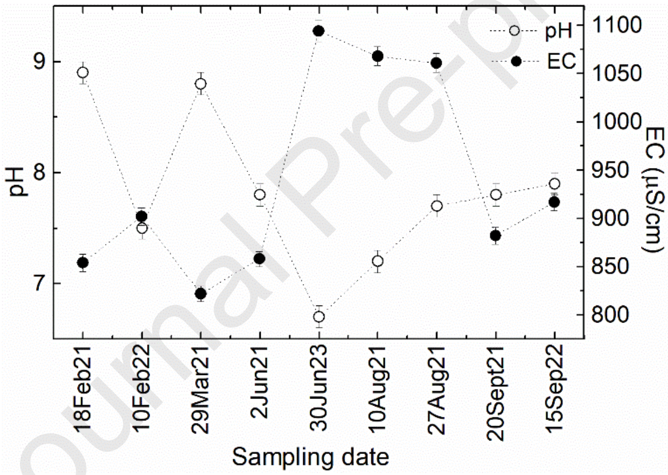


Fig. 4. Parameters of the stream water: (a) pH and (b) EC.

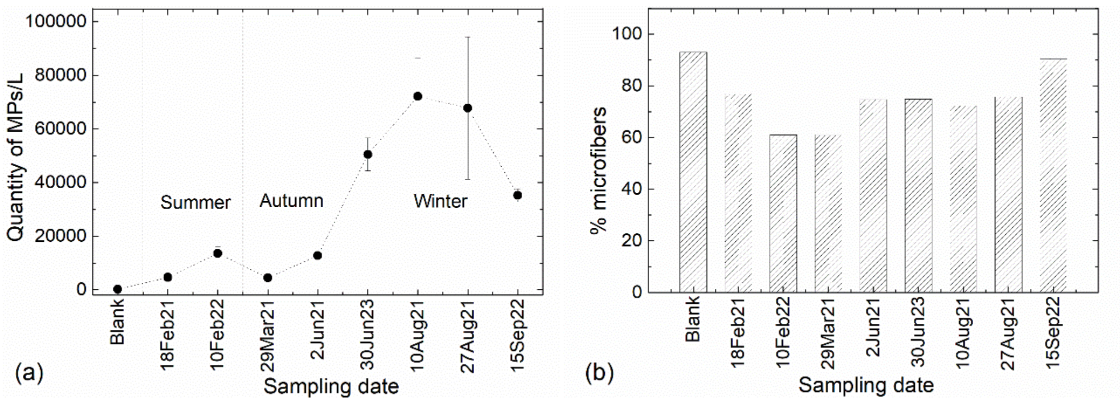


Fig. 5. (a) MP concentration in the stream water on the different sampling dates. (b) Percentage of microfibers found in each sampling.

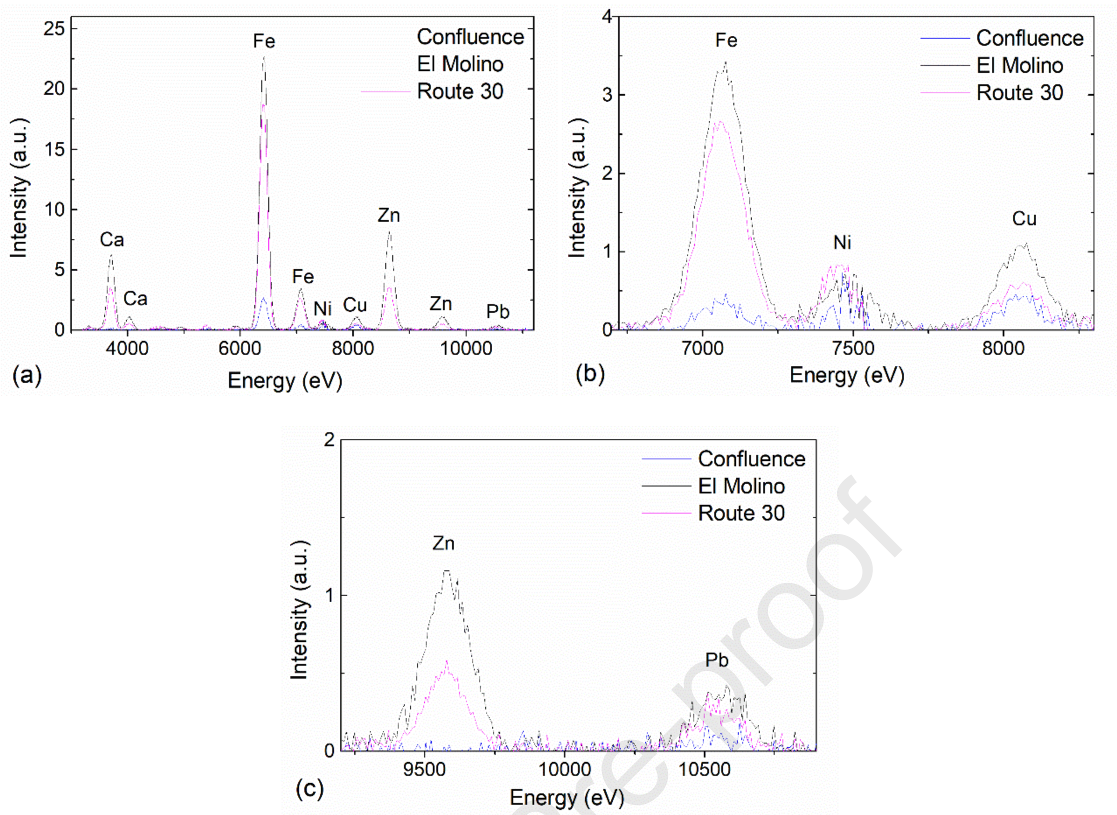


Fig. 6. (a) X-ray fluorescence spectra corresponding to MPs extracted from different extraction points in the sampling of August 10, 2021. (b) and (c) are magnifications of different regions of the spectra.

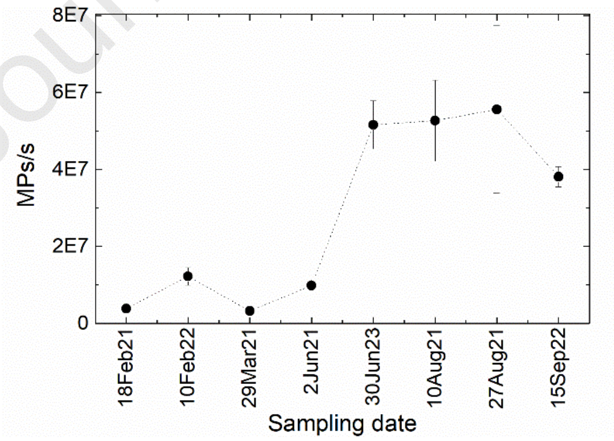


Fig. 7. MP flow in the stream water considering the stream flow for each sampling.

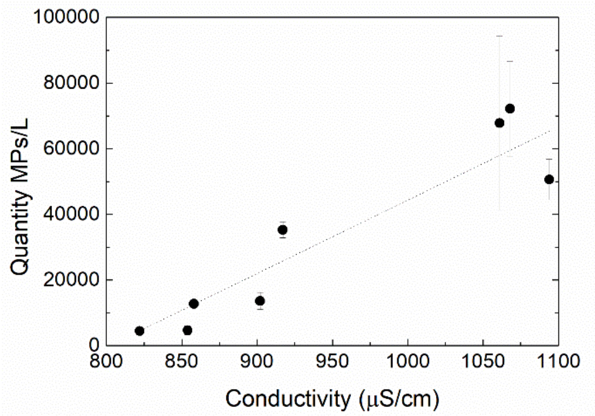


Fig. 8. MP concentration in the stream water versus EC.

Figures caption

Fig. 1. Map of the Langueyú stream from its source to the intersection with Route 30, located in Tandil, Buenos Aires province, Argentina. WWTPs discharges and extraction points are shown. Images were adapted from Google Earth, June 2022, https://earth.google.com.

Fig. 2. Stream flow for each sampling date.

Fig. 3. (a) Historical monthly temperatures, T_{max} and T_{min}, and the measured temperature of the stream water for each sampling date, T_w. (b) Historical accumulated monthly precipitation (30 days (1991-2020)) and accumulated precipitation 2, 5 and 10 days before each sampling date.

Fig. 4. Parameters of the stream water: (a) pH and (b) EC.

Fig. 5. (a) MP concentration in the stream water on the different sampling dates. (b) Percentage of microfibers found in each sampling.

Fig. 6. (a) X-ray fluorescence spectra corresponding to MPs extracted from different extraction points in the sampling of August 10, 2021. (b) and (c) are magnifications of different regions of the spectra.

Fig. 7. MP flow in the stream water considering the stream flow for each sampling.

Fig. 8. MP concentration in the stream water versus EC.

Fig. S1. Average climatological values 1991-2020 in the city of Tandil. Left: precipitation. Right: Maximum and minimum temperature. The data were extracted from ref. (SMN, 2023).

Highlights

- The highest microplastic concentrations were measured in winter (dry season).
- There is no direct consequence of precipitation with microplastic concentration.
- Discharges from the plants cause changes in the stream water (conductivity and pH).
- Conductivity would serve as an indicator of the microplastic concentration.
- Metallic contaminants were found adhered to the microplastics.

CRediT author statement

Susana Montecinos: Conceptualization, Methodology, Investigation, Writing – Original Draft.

Sebastián Tognana: Conceptualization, Methodology, Investigation, Writing –Review & editing.

Walter Salgueiro: Writing –Review & editing.

Carlos Frosinini: Validation, Formal analysis, Writing –Review & editing.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: