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Characterization of Microplastics in Total Atmospheric Deposition Sampling from Areas Surrounding Industrial Complexes in Northwestern Colombia

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Abstract: In this study, the total atmospheric deposition of microplastics in places near an industrial complex in Cartagena, Colombia is evaluated by taking samples at three points at different distances from the industrial zone. The samples obtained were treated to quantify and identify the type of plastic present, indicating the presence of polystyrene, polypropylene, polyethylene, polyvinyl chloride, and polyethylene terephthalate. The values of microplastics obtained were related to the climatic conditions of the areas (wind and rainfall) to determine these effects on the transport of microplastics. Values of 9472 $\pm$ 702 MP were obtained at the point closest to the industrial area and 1455 $\pm$ 14 MP at the farthest point, within which a greater proportion were fibers. In this study, it was also possible to determine that the microplastics most affected by the wind were the fragments.

Keywords: microplastics; pollutions; polypropylene manufacturing; atmospheric pollutions; polymers

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1. Introduction

Plastic pollution, and mainly that related to the generation of microparticles or microplastics (MP), has increased scientific, academic, governmental, and general public concern worldwide [1,2]. Its increase has been associated with the exponential increase in the production and transformation of polymers and their derivatives. MPs are made up of plastic particles with sizes between 1 and 5 µm, and their size reduction caused by physicochemical or mechanical factors gives rise to nano plastics with sizes less than 1 µm [3]. The presence of MP in different ecosystems has been documented by other authors, being identified in air, groundwater, sediments, soils, etc. [4–6] The presence of MP in these ecosystems is favored by their small size, which facilitates their transport by the dynamics of the environment (e.g., winds, precipitation, rivers); MP can circulate longer in the air as a result of its low density [7].

It has been shown that MP can be generated by the degradation of materials such as clothing, children's toys, worn car tires, bicycles, etc. [7] aspects that are independent of the country, city, or geography. Therefore, these can be present in different countries. In fact, the presence of MP has been noted in the United Kingdom, France, China, in some urban areas in the United States, the Atlantic Ocean, and in some national parks, among others [7–10]. However, the investigations are not focused on exploring MP profiles in areas near petrochemical plants, and their information is scarce. The study of the effects of petrochemical plants, especially those associated with the production of polymers, is necessary so that medium-sized, small, and large companies can be regulated and/or required to adapt and optimize processes that guarantee sustainable development and a healthier environment for the surrounding communities, in addition to allowing the determination of the contribution of these plants to the increase of MP in the environment.

In Colombia, there are several plants near bodies of water and residential areas that produce different types of plastics, such as polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyethylene (PE), polystyrene (PS), and others focused on the transformation of these polymers and others that are synthesized differently, with a production of thousands of tons per year. In these plants, investigations on contaminants of interest to the process have been carried out, allowing the fundamental role in the environmental impact to be determined [11–18]. However, the identification of contaminants in the process can damage a batch, generating waste that is easily degradable and can generate microplastics and, due to its origin, can contain chemical additives such as bisphenols, plasticizers, phthalates, and brominated flame retardants that have serious health consequences as they are endocrine disruptors [19,20], in addition to pollutant residues from industrial processes that can be released into the environment due to the decomposition of MP in the air, causing a public health problem [21–23].

In this work, MPs are identified and quantified in areas surrounding petrochemical plants in Cartagena, Colombia. An evaluation of the amount of MP deposited per square meter on roofs was also conducted. A classification of microplastics was also made according to their shape and according to the type of polymer found by differential scanning calorimetry DSC.

2. Materials and Methods

2.1. Sampling of Total Atmospheric Deposition

The samples of interest were collected between January and December 2021 on the roofs of 3 buildings of family homes in the areas surrounding the industrial sector of Cartagena-Bolívar (approximately 20 m above the ground) at three different points (Figure 1). Dry and wet samples of total atmospheric deposition were taken using five stainless steel funnels and five 5-L glass flasks. To carry out the sampling, the funnels were connected to the top of the jars to guarantee the entry of the sample and its loss.

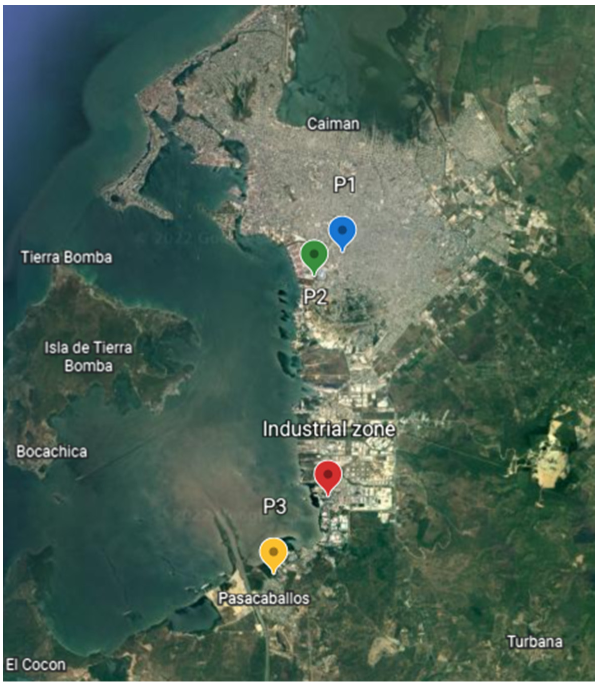

Figure 1. Map of the sampling points.

The funnels were cleaned three times with Milli-Q ultrapure water (18.2 MΩ·cm) to recover any radioactive fibers that may have adhered to the funnel walls. For two weeks, there were five rain events with a total rainfall of 38.1 mm, and a total of 5.4 L of rainwater was collected (Figure 2). Rainfall intensity and other meteorological data were continually collected and used in the computations by a meteorological station at the same sample site [24].

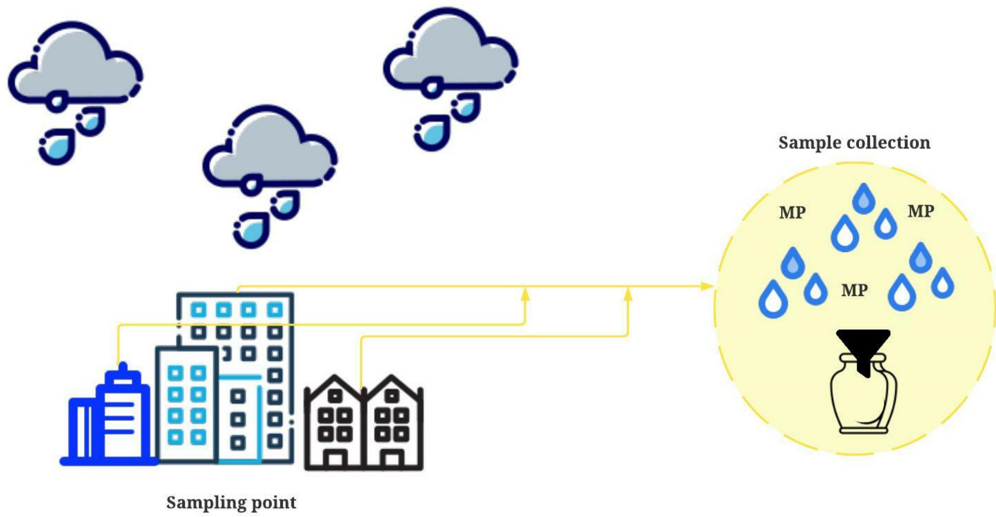

Figure 2. Sample collection.

2.2. Preparation of Samples for Analysis of Microplastics

To avoid cross-contamination and interference in the identification of microplastic particles, preventive measures were applied:

1. Aluminum foil and glass Petri dishes were used to isolate the samples from the environment and for storage. To minimize contamination from airborne plastic particles, samples were always wrapped in aluminum foil or housed in glass Petri dishes.
2. For the collection of samples and their storage, no plastic material or any of its derivatives is used. The bottles, funnels, and other materials were made of glass.
3. All the working materials were always washed with Milli-Q ultrapure water (18.2 MΩ·cm) five times before use.
4. All the tests carried their respective blanks. To guarantee that there was no type of cross-contamination and each analysis of a sample blank, the same treatments mentioned in the points before this numeral were always performed [3,10].

The analysis of these types of environmental samples is always subject to the presence of organic material or bacterial growth, so these samples were treated with 30% W/W hydrogen peroxide.

2.3. Sample Processing

The organic content present in the sample was removed by adding peroxide (20 mL per liter of sample) and stirring for a period between 12 and 24 h at 60 °C. To guarantee a particle size of 10 to 5000 µm, sieves and polycarbonate membrane filters were used. In addition, a solution of rose Bengal was used on the filter and allowed to react for 10 min to prevent particles of materials other than plastics from being quantified. After this time, the filters were washed with pure water and dried at 60 °C.

2.4. Quantification of the MPs in Samples

On a filter, two subsamples of about 300 mm^2 and 250 mm^2 were picked from the total air deposition samples and quantified using a Lecia Zoom 2000 stereo microscope to count the large particles along with the fibers and follow the categorization criteria. Harmann et al. (2019), which indicate that in order to identify a microparticle as a fiber, it must be flexible and have a constant thickness, and the organic and cellular structures must not be visible to be considered artificial fibers. For the classification of the MP, it was defined that microparticles with a thin and flat shape are categorized as films, those with a spherical shape as spheres, and those that did not have a specific pattern would be classified as fragments or irregular. A WITec Raman confocal microscope was used for small particles. In the visual count, factors that could affect detection, such as color, were considered. The calculation of the total deposition rate was performed using equation 1, where Nsub refers to the number of particles collected in the subsample, Af to the filter area (1735 mm^2), Asub is the filter area of the subsample, AS the sampling surface area, and T is total sampling time [24].

$$\text{Deposition rate (MP m}^{-2}\text{ day}^{-1}) = (\text{Nsub} \times \text{Af})/(\text{Asub} \times \text{AS} \times \text{T}) \quad (1)$$

2.5. Thermal Analysis

The polymers that were part of the samples were identified by determining their melting points by DSC using the DSC Standard Cell RC kit. Heating the samples to 280 °C and then cooling them to 0 °C at a rate of 10 °C min^{-1} [25–28].

3. Results

3.1. Total Atmospheric Deposition

The quantification by visual means allowed the quantification of red, blue, and gray microplastics. These colors, together with the shape and type of material, can help determine the origin of the microplastic [29]. Although other authors have identified transparent microplastics, in our case it became difficult due to the implementation of white filters, so it cannot be determined whether or not there was a presence of transparent plastics. Using microscope quantification, it was possible to determine the MP deposition in areas surrounding petrochemical plants, obtaining values of 2259 ± 84 for fibers, 1177 ± 57 for films, and 859 ± 79 for fragments deposited on ceilings in sampling point 1 (P1). For sampling point 2 (P2), MP values deposited on restaurant roofs of 5687 ± 978 for fibers, 2060 ± 154 for films, and 1725 ± 150 for fragments were obtained. And on the roof in sampling point 3 (P3), values of 573 ± 52 were obtained for the fibers, 364 ± 64 for the films, and 517 ± 79 for the fragments. The total MP found in the three points shows a marked trend, which shows that as the sampling point moves away from the industrial zone, the value of total MP decreases depending on the direction of the wind. Total MP values were 9472 ± 702 in P2, which was the highest value, 4295 ± 14 in P1, and 1455 ± 14 in P3.

Average deposition rates were calculated, obtaining values for fibers during the sampling period of 537.5 × 104, 1031.2 × 104, and 138.6 × 104 fibers m^{-2} per day at point 1, point 2, and point 3, respectively. The average deposition rates of films were lower with respect to fibers at 168.5 × 104, 293.2 × 104, and 51.6 × 104 films m^{-2} per day at point 1, point 2, and point 3, respectively. At points 1, 2, and 3, the average deposition rates of the fragments were 125.5 × 104, 247.2 × 104, and 75.6 × 104 fragments m^{-2} per day, respectively. The results of this research were compared with other studies carried out in different parts of the world, and it was shown that the values obtained in this study exceed the rates obtained by other authors. When compared with the rate obtained in the center of London, it is observed that the values of this study are approximately 4.2 and 7.36 times higher than the one they obtained [7]. In Paris, they obtained a rate of 110 ± 96 MP m^{-2} per day, which would be 38.48 times smaller than that found in this work [10]. Similar studies were conducted in Dongguan, China and the concentration areas in the western United States, obtaining rates of 36 ± 17 and 132 ± 6 MP m^{-2} per day [9], these results indicate that the area where the study is carried out will also determine the amount of microplastics that may be in the environment [30]. However, it should also be borne in mind that the climate, wind direction, commercial development, and other factors can affect the amount of MP present in an area. To determine this, the values of precipitation and wind speed were recorded over sampling time and were compared with the MP records as shown in Figure 3.

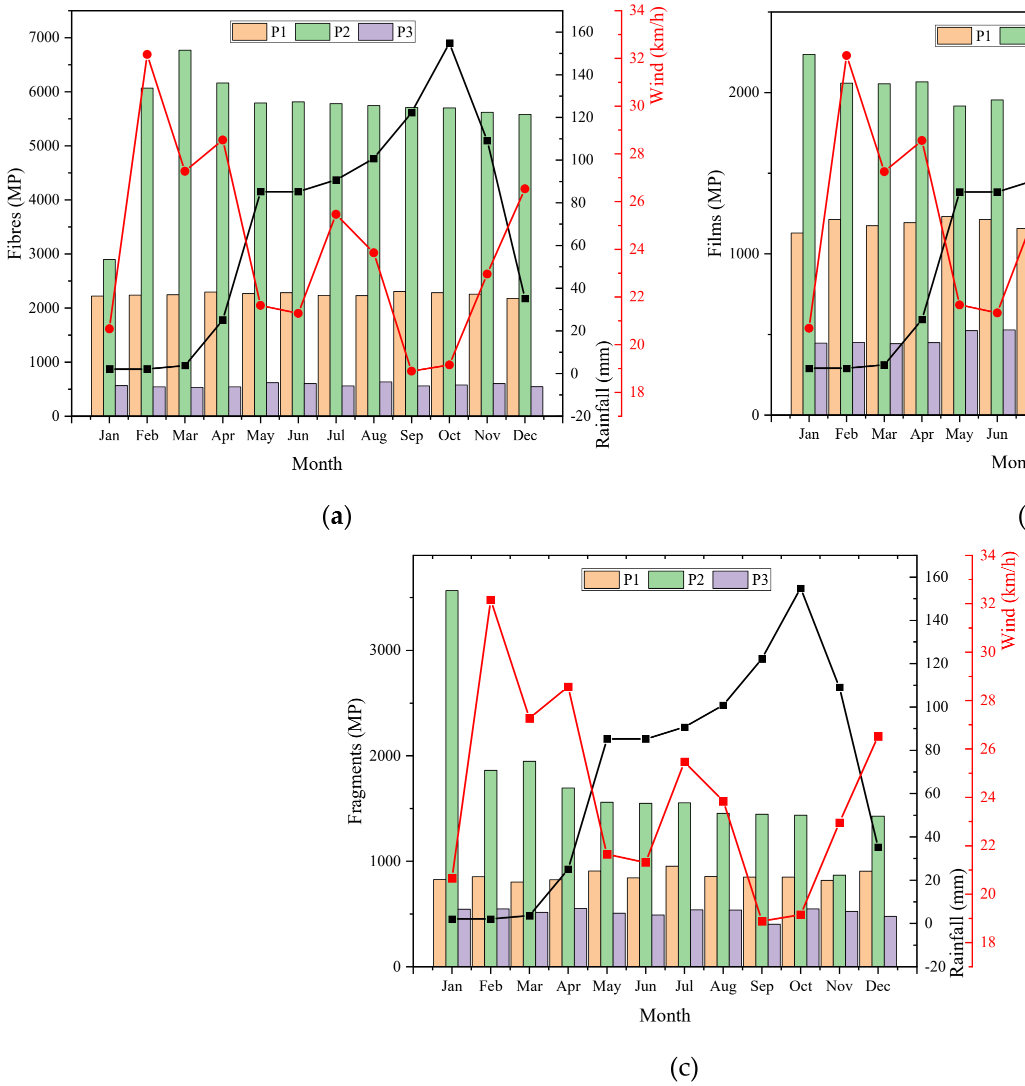

Figure 3. MP variation with respect to the month, wind speed, and rainfall. (**a**) fibers; (**b**) films; and (**c**) fragments.

When analyzing the data obtained and relating them to the variation of wind speed, wind direction, and rainfall presented, it was determined that they are factors that influence the amount of microplastics. The rain allows the collection of PMs at the sampling points, so if there is little rainfall, the amount of PMs sedimented on the roofs can be reduced. In the case of the wind, this allows the transport of the particles, so its speed and direction will influence the distribution of the microplastics [31–33]. Regarding the type of microplastics (fragments, films, or fibers), it was observed that the wind has a great incidence. This is because the shape of the PM allows it to join other particles, increasing its contact surface with the air and its weight, which are important factors in the transport of particles. It is important to highlight that the direction of the wind is a variable that must be considered for the dispersion of MPs [34–36]. In this case, the highest concentrations of microplastics occur in the north, which is the predominant direction of the wind in the city of Cartagena. What allows accumulation on roofs is precipitation. If there is a lot of rain, there is a high probability that the MPs end up in bodies of water since they are dragged by the resulting water currents. But if the rainfall is low, there are no water currents that drag them, so they accumulate where they fall.

3.2. Identification of Plastics by DSC

Representative samples were taken from each sampling point to identify the microplastics that were found. Figure 4 shows the DSC of the plastics identified at the different points. Through this analysis, five different plastics were identified in most of the samples, which was expected due to the proximity between the points and the commercial activities that take place in the area, with small variations between the concentrations of the identified plastics.

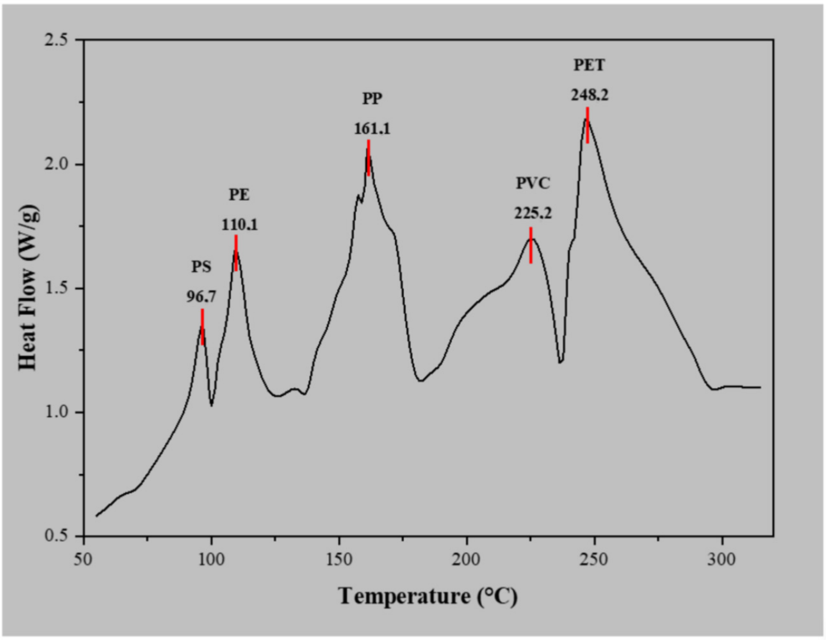

Figure 4. DSC of the identified plastics.

The identified plastics correspond to polystyrene (PS; $(C_8H_8)_n$), which is used in the production of disposable plates and sound insulation material, among others; low-density polyethylene (PE; $(C_2H_4)_n$), which is used in personal hygiene products, in films for food packaging, some textiles, etc.; polypropylene (PP; $(C_3H_6)_n$), which can come from synthetic fibers used in textiles, containers, etc.; polyvinyl chloride (PVC; $(C_2H_3Cl)_n$), which is used as a packaging material, in textiles, cleaning materials, insulation for cables, pipes, etc. and, finally, polyethylene terephthalate (PET; $(C_{10}H_8O_4)_n$), was identified, which is used for the manufacture of bottles and synthetic fibers for textiles. These plastics are produced by plants in the industrial zone; however, they can also come from the degradation of plastic waste in the city. These materials have marked melting temperatures that allow their identification and are widely identified when microplastics are analyzed because they are present in many objects that are constantly used, either because they were designed that way (e.g., microplastic spheres for scrubs) or because of wear and tear. deteriorating, giving rise to microplastics.

4. Conclusions

This scientific study investigates the presence of microplastics on the roofs of houses near the industrial zone of Cartagena, Colombia, to determine if the proximity to an industrial complex increases the concentration of microplastics in the environment. Obtaining the distribution of microplastics with respect to the industrial zone is due to climatic factors such as wind (speed and direction) and precipitation occurring in the area. This is because the wind influences the transport of the particles, determining their distribution in the different areas around the industrial complex, and the precipitation helps to concentrate them at different points. However, in the case of Cartagena, rainfall was scarce during the year of study, which caused an accumulation of microplastic deposition at the point of fall since they are not carried away by water currents formed by rainfall. The microplastics present in the atmospheric depositions were also identified to determine which ones have the greatest incidence in the area, which allows us to know which petrochemical plants contribute the most to microplastic pollution, considering that in the industrial zone there are several petrochemical plants that produce the different plastics identified, in addition to the pollution contributed by plastic waste.

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