Microplastics from degradation of tires in sewer networks of the city of Riobamba, Ecuador

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ABSTRACT

Microplastics are small synthetic particles that come from petroleum derivatives, are difficult to degrade and their origin is found in industrial activity and domestic consumption, even in tires. The presence of small particles (0.1 μm to $< 5\text{ mm}$) of plasticizer Bis (2-ethylhexyl) phthalate (DEHP) and synthetic rubber, which due to their size and origin are called microplastics. The friction occurs between the asphalt in contact with the tires of cars generate the detachment of small residues of it, these residues come to contain a DEHP element. Simple residual water samples were carried out in the different sewage collectors in Riobamba city, 250 mL of each of these samples were filtered using vacuum suction equipment, to then examine the filters with a visual microscope. Obtaining as a result that 80% of the samples taken and analyzed in the laboratory contain the clear presence of DEHP plasticizer from the friction of tires (confirmed by the Principal Component Analysis) with the asphalt of the streets of the city of Riobamba, and that only 20% of the samples analyzed do not present DEHP plasticizer of this type, generating a medium risk for the health of humans and aquatic animals in the sector.

Keywords: Additive, Microcontamination, Microplastics, Plasticizer, Tires

1. Introduction

Since the sixties of the last century the production of plastics has grown almost 9% each year. In 2015, 322 millions of tons were produced according to UN data. Later part of plastic ends in the environment, particularly in the marine environment, around eight million tons per year [1]. The water, microorganisms and sunlight break down the plastic until is reduced to small particles of a few microns in length [2]. Some are so small that they are ingested by marine organisms due to their similar size with microplankton, and microplastics (MPs), also contain attached organic pollutants [3]. MPs are small synthetic particles that come from petroleum derivatives, are difficult to degrade and their origin is in industrial activity and domestic consumption, being present in detergents, toothpastes, salt, in skin products such as exfoliants and sunscreens and even many synthetic fibers from clothing and tires [4]. The problem is that these materials

are toxic, abrasive and difficult to treat due to their small size [5]. But the question that science must still answer is from what amount ingested plastic can be a problem for human health. There are two risks, on the one hand the impact of the physical presence of plastic particles and, on the another, the possible toxicity of its chemical components. Studies carried out like "Orb Media", in collaboration with the Universities of New York and Minnesota, they determined that MPs are omnipresent in the human food chain. According to this study, it was possible to detect the presence of MPs in the feces of people who lives in Europe, Russia and Japan, different types of plastic were found in eight volunteers from this pilot study, presented during a gastroenterology congress in Vienna as a world first [6]. For a week, five women and three men, ages 33 to 65, residing in Finland, Netherlands, Great Britain, Poland, Italy, Russia, Japan, and Austria, wrote down what they ate, the size of the plastic samples found in their stool varies from 50 to 500 micrometers, more or less the thickness of a hair.

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Currently assumed they were ingested through seafood that the volunteers consumed, but also from the water in plastic bottles, drinks, or food wrapped in plastic [7]. These products correspond to daily consumption and are in contact with water, the bad disposal of waste also causes large amounts of MPs to be poured into the sewer system [8]. The MPs found in drinking water collection and distribution networks in the city of Riobamba are a constant concern, since the presence of this contaminant in water resources is evident [9]. That is why the concern becomes bigger. In Riobamba city due to the presence of an increasing vehicular flow, the friction between the asphalt in contact with tires of the cars generates the detachment of small residues of it, these residues come to contain an element called plasticizer of di (2-ethylhexyl) phthalate (DEHP) [10], this is a chemical polymer in liquid state derived from petroleum, is commonly added to plastics to make them more flexible, this additive is incorporated in the manufacturing process of the tires and turns out to be very harmful for the ecosystem and for the human being since it is a genotoxic, carcinogenic element [11]. 60% of synthetic rubber and 75% of natural rubber is used in the manufacture of tires and related products [12]. According to data provided by Beliczky and Fajen, the type of rubber used for the manufacture of tires until the year 1993 is natural rubber, however this was modified and currently polymers are used as: Styrene-butadiene (SBR), Polybutadiene (BR), and in very few quantities Polychloroprene (CR), which being modified compounds are more difficult to degrade and whose problem is the chemicals and other elements added as DEHP type plasticizers [13]. This additive is compatible with CR, SBR and BR type rubbers, the most widely used rubber families in the tire industry. The friction between the asphalt in contact with the tires of the cars generates the detachment of small residues [14]. Adding of physical factors such as wind [15] and water tend to move into gutters and mix with domestic and industrial wastewater and in the end may appear in the various sewer systems, there is direct contact of these waters with the biological environment becoming a major problem for the habitants of the city [16]. Therefore, the aim is to determine the percentage of source

MPs from friction-degraded tires in sewer systems with the city of Riobamba as a case study.

2. Materials and Methods

The study area is located in the city of Riobamba, for which it coordinated with the Municipal Company of Potable Water and Sewerage of the city of Riobamba (EP EMAPAR), which provided the respective information of the sewerage networks that exist in the city. There are 41 sewage discharges, however for this investigation 28 discharges are discarded that are purely domestic since they do not have contact with tire waste, resulting in 12 sampling points in which different water samples were taken in order to detect the presence of microplastic from tires in them.

2.1. Sample Calculation

The sample size was made with data obtained from the Department of Vehicle Registration - Directorate of Mobility, Traffic and Transport Management of the GADR, 2019, which provided the exact number of vehicles registered for the year 2018 and 2019. However, as the current year was not yet over, it was considered to use the data on the number of vehicles registered for 2018 for this research. For the year 2018 the total number of vehicles registered in the city of Riobamba was 48,747, this numerical value is considered as our population to analyze. To calculate the number of samples to be analyzed [17] we used the sample size Eq. (1).

$$sample\ size = \frac{\frac{z^2 \cdot p(1-p)}{e^2}}{1 + \left(\frac{z^2 \cdot p(1-p)}{e^2 \cdot N}\right)} \quad (1)$$

N = population size,
e = margin of error,
p = probability of success,
z = z-score

Table 1. Discharges of Sewage Tributaries to Receiving Bodies

No	Coord. x	Coord. y	Receiving Body	Location	Observations
1	758,451	981,5576	Chibunga river	185 m from the municipal greenhouse	Waste water discharge
2	758,622	981,5549	Chibunga river	Urb. Agrotouristic farms	Dry
3	759,411	981,5244	Chibunga river	Quinta Macaji	Waste water discharge
4	759,495	981,5101	Chibunga river	Under the Batan bridge	Dry
5	759,775	981,4766	Chibunga river	60 m before the pte. La Primavera	Covered
6	759,917	981,3889	El bunque ravine	120 m before the pte. Yaruquies	Dry
7	759,954	981,3895	El bunque ravine	80 m before the pte. Yaruquies	Waste water discharge
8	761,719	981,2859	Chibunga river	At the end of the ecological park	Waste water discharge
9	758,925	981,3246	Puctus ravine	Street extension Pedro Duchi	Waste water discharge
10	758,595	981,9220	Las abras ravine	At the end of the coop. Diocesis	Dry
11	758,678	981,9059	Las abras ravine	At the end of the Sector the Providencia	Impossible access
12	758,718	981,8837	Las abras ravine	15 m from the pte. From the urb.Caminos del Sol	Impossible access
13-42	—	—	Chibunga river	Between bridge La Primavera individual houses	Household water discharges only

After applying the equation with a 95% confidence level, 51 samples were obtained for analysis. There are 12 sewerage distribution networks available for sampling, it was decided to take 5 samples from each distribution network as shown in Fig. 1 at different times to obtain a reliable laboratory result. Field visits were made to all 12 sewerage discharge points to find out the conditions in which they are located.

2.2. Sample Collection and Processing

The water quality standard was used for sampling. Sampling. Part 3: Conservation and handling of water samples [18]. A field card

was used for each wastewater sample taken, in order to facilitate the data collection and verify the correct process given for the sampling, which consists of the following data: letterhead of the educational institution, geographic coordinates, date, name of the sewage system, among other data. Once the samples have been taken, they are analysed using the synthetic mycoparticle detection methodology proposed by Paredes et al. [9], in which a vacuum suction pump was used for the purpose of filtering the waste water, as opposed to the Rose Bengal was not used for this research since the tyres contain "black carbon" which is detected by the visual microscope without the need for a dye that gives the MPs

Fig. 1. DEHP plasticizer present in APR-2 sewerage water samples (Quinta Macají). Zoom 4,8:1.

Fig. 2. DEHP plasticizer present in APR-3 sewerage water samples. Zoom 4,8:1.

Fig. 3. DEHP plasticizer present in sewage water samples Batán. Zoom 4,8:1

Fig. 4. DEHP plasticizer present in the samples of sewage water collector Emisario Chibunga. Zoom 4,8:1.

Fig. 5. DEHP plasticizer present in the Yaruquies sewage water samples. Zoom 4,8:1.

refractoriness. DEHP particles were degraded to compare them with those obtained in the samples and were processed through a 2-4 μm pore filter. In the laboratory we proceeded to pour out 250 mL of water sample by vacuum filtration through a cellulose filter of 37 mm diameter with a pore size of 2 to 4 μm , then this filter was placed in a labeled Petri dish. After a drying time of 5 min, a Visual Microscope (iVu 7000. With 7.1 Mpx) with an integrated camera was used to check for the presence of MPs which according to [18, 19], are set in sizes from 5 mm to 1 μm . Once the results of this procedure were analyzed and the MPs from the tire degradation were identified, the number of filters containing these contaminants was recorded in order to calculate the percentage of samples with MPs.

2.3. Data Analysis

Data analysis was conducted using IBM SPSS Statistics Version 20. Principal component analysis were computed for source identification.

3. Results and Discussions

For the investigation we took into account what was indicated by Rojo Nieto & Montoto [19], who establish that the classification of plastic particles according to their size is of a range between 5 mm to 1 μm to denominate it microplastic, it should be taken

into account that the analyzed samples are experimental samples that contain elements considered as DEHP type plasticizers from 2 to 6 field units and other polymers such as CR, BR, SBR, for every 250 mL of filtered water as indicated below.

3.1. Presence of DEHP Plasticizer in Collectors

The following data were obtained for the APR-2 collector, APR-collector, Batán collector, Emisario Chibunga collector and Yaruquies collector, whose wastewater discharge is to be deposited in the waters of the Chibunga River.

Depending on the number of particles found in water sources, is relatively low according to [2], not aggressive to human health, but the samples 4 are dangerous for marine animals such as fish, shellfish, bivalves or others [20]. Comparing mean results (1.6 ± 1.4 MP/ 250 mL to 3 ± 2.19 MP/250 mL) obtained with other studies which adopted similar method as this study, lower concentrations were reported in Finland 1 ± 1.1 MP/L [21] and $0.04 - 1.2$ MP/L [22]. Further, it was higher than concentration reported in the US, 0 MP/L [23] while lower to the ones reported in Netherland 65 ± 67 MP/L [24]. After the results obtained, it can be said that 80% of the samples taken and analyzed in the laboratory contain the clear presence of DEHP Plasticizer from the friction of tires with the asphalt of the streets of Riobamba City, and only 20% of the samples analyzed do not present DEHP Plasticizer of this type. The data obtained after the observation of the filters with the visual microscope (iVu 7000. With 7.1

Table 2. Data, Presence of DEHP Plasticizer in Collectors

Sample No.	Collector	Receiving Body	Collector's Section	Presence Of Plasticizer Dehp		
				Field units (No. of particles/ 250 mL)	YES	NO
M1	APR-2	Chibunga river	1.8 x 1.5 m	3	X	
M2	APR-2	Chibunga river	1.8 x 1.5 m	3	X	
M3	APR-2	Chibunga river	1.8 x 1.5 m	6	X	
M4	APR-2	Chibunga river	1.8 x 1.5 m	4	X	
M5	APR-2	Chibunga river	1.8 x 1.5 m	3	X	
M6	APR-2	Chibunga river	1.8 x 1.5 m	0		X
M1	APR-3	Chibunga river	1.8 x 1.8 m	0		X
M2	APR-3	Chibunga river	1.8 x 1.8 m	4	X	
M3	APR-3	Chibunga river	1.8 x 1.8 m	4	X	
M4	APR-3	Chibunga river	1.8 x 1.8 m	0		X
M5	APR-3	Chibunga river	1.8 x 1.8 m	2	X	
M6	APR-3	Chibunga river	1.8 x 1.8 m	2	X	
M1	Batán	El Bunque ravine	200 mm	0		X
M2	Batán	El Bunque ravine	200 mm	3	X	
M3	Batán	El Bunque ravine	200 mm	2	X	
M4	Batán	El Bunque ravine	200 mm	0		X
M5	Batán	El Bunque ravine	200 mm	2	X	
M6	Batán	El Bunque ravine	200 mm	3	X	
M1	Emisario Chibunga	Chibunga river	700 mm	2	X	
M2	Emisario Chibunga	Chibunga river	700 mm	2	X	
M3	Emisario Chibunga	Chibunga river	700 mm	0		X
M4	Emisario Chibunga	Chibunga river	700 mm	5	X	
M5	Emisario Chibunga	Chibunga river	700 mm	6	X	
M6	Emisario Chibunga	Chibunga river	700 mm	3	X	
M1	Yaruquies	Puctus revine	1.2 x 0.9 m	2	X	
M2	Yaruquies	Puctus revine	1.2 x 0.9 m	3	X	
M3	Yaruquies	Puctus revine	1.2 x 0.9 m	3	X	
M4	Yaruquies	Puctus revine	1.2 x 0.9 m	4	X	
M5	Yaruquies	Puctus revine	1.2 x 0.9 m	2	X	
M6	Yaruquies	Puctus revine	1.2 x 0.9 m	3	X	

Mpx), and calculated the percentages of DEHP type plasticizers, we have the result of plasticizing element together with the various polymers (SBR, BR, and CR), used for the manufacture of tires in the stages of mixing compounds in Banbury malaxator and vulcanize [25], due to their degree of toxicity, their stony origins, their method of manufacture and their sizes (between 0.5 and 2 mm) are considered as secondary MPs, since they come from the decomposition and fragmentation of a macroplastic that is the tyre [22]. Any type of microplastic or macroplastic structure presents a great risk to the health in animals and people [5]. Even more when a city like Riobamba doesn't have a water treatment plant.

3.2. Source Identification- Principal Component Analysis

To determine the precise source(s) of particles in the sewage water; we conducted a principal component analysis following standard procedures [26]. We used the varimax rotation with Kaiser Normalization because it better explained the possible groups or sources that influence the system and maximize the sum of the variance of the factor coefficients [26]. The factor loadings for particles in rotated space are shown in Fig. 6. Two components were extracted based on eigen value > 1, best described the sources.

According to [26] and [27], components loadings values of > 0.75, 0.75-0.50, and 0.50-0.30 were classified as "strong", "moderate", and "weak", respectively. The PC1 explained 41.423%

Fig. 6. Principal Component Matrix using varimax rotation of particles in the sewer water from different points. MG: 185 m from the municipal greenhouse; QM: Quinta Macaji; YU: 80 m before the pte. Yaruquies; EP: At the end of the ecological park; PD: Street extension Pedro Duchi.

of total variance and was found to be positively correlated to MG, QM and YU (0.094 to 0.969) while PC2 explained 28.935% of total variance with weak correlation to PD and EP. Overall, most (60%) of the study points showed positive relating to degradation of tires from road frictions. Other likely source(s) could be from atmospheric deposition [15], which may account for the other 40% in PC2.

4. Conclusions

Based on the results obtained in the investigation, after collected and analyzed 30 wastewater samples in different sewage collectors in Riobamba city, is established that in 24 of the samples analyzed there is evidence of the presence of MPs, which represents 80% of the total samples analyzed in the laboratory. Since there are no standardized parameters for the amount of microplastics allowed to be discharged into water bodies, but based on toxicity studies carried out by different organizations, it can be concluded that the amount and type of MPs found in the samples analyzed represent an average risk to the health of animals living in aquatic environments as well as to humans. In addition, the lack of standardized parameters and specific techniques for identifying MPs makes it difficult to establish the chemical and physical properties of the particles found, which is why it was not possible to give a high degree of reliability to the results obtained. Further research should apply other methods for the characterization of microplastics in which the chemical properties of each particle found can be identified. The source of contamination of wastewater with MPs comes from the substitution of natural rubber by synthetic rubber (SBR, CR and BR) in the manufacture of tires as well as the use of different additives such as DEHP type plasticizers, oil-based polymers that are toxic and carcinogenic. It should be noted that

the samples that do not present data on the amount of DEHP plasticizer were taken in the morning on days with little rain, which is a possible cause of not finding contaminating elements in these samples, since the residues that are released from the tires tend to remain on the asphalt of the street and others due to density are displaced by the wind, while other less dense elements remain in the asphalt and are transported to the gutters by the action of rain and end up being mixed with wastewater, which is why only residual water discharges - rainwater - were analysed and purely domestic discharges were ruled out. The presence of MPs in the Riobamba sewer system from the friction of the tire with the asphalt is totally evident, which shows the risk that exists when there is no control of them since the different companies that manufacture these tires do not report the content that their products have and the possible risk that can be generated for the environment and living beings.

Author Contributions

M.P. (Professor), director of the research project and author of the research lines. R.V. (Associate external Professor) wrote and revised the manuscript. T.C. (Professor) wrote and revised the manuscript. C.C. (Engineering student) experimental trials. C.E.E. (Associate external Professor) wrote and revised the manuscript.

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