Revista de Chimie
https://revistadechimie.ro
https://doi.org/10.37358/Rev.Chim.1949

Year-Round Behavior of Micro-plastics in Coastline Sand

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Abstract: *This article aims to identify the behavior of light and heavy micro-plastics on the southern shore of the Caspian Sea during different seasons of the year. For this purpose, data from 15 sampling stations were gathered in four seasons, and subjected to various analyses after the samples were prepared. To separate light and heavy micro-plastics, the samples were washed with water. Analysis of TGA-DSC and FTIR imaging was used to quantitatively and qualitatively identify microplastic samples and optical microscope images were used to quantify the number of particles. According to the results, the amount of light microplastics in the spring and winter is less than in the summer and autumn. In the spring, the highest levels of pollutants are PVC, PES, PET and PU. In the summer and autumn, the values of PE, PP, PA, PAT, PU and PVC are at a relatively equal range. In the winter, most pollutants are PVC, PES, and PU. In conclusion, PE, PP, PPA, and PET should be removed from the environment before they can be modified by physical and chemical processes.*

Keywords: *coastline, FTIR imaging, micro-plastic, TGA-DSC*

1.Introduction

The Caspian Sea is the largest lake on Earth with an area of 400,000 square kilometers, more than five times the size of Lake Superior, one of the largest lakes in the United States [1]. Hence the Caspian is known as a sea because of its large size. The Caspian Sea is also at the crossroads of the Middle East, Europe and Asia in highly strategic areas, but has now become one of the world's most polluted seas. The most important sources of pollution in the Caspian Sea are land and sea pollution, oil and gas resources, water level fluctuations and human factors [2]. On the other hand, pollution has increased in the Caspian Sea as oil production and sea transport increase. In addition, drilling, pipeline leakage, oil rigs and natural oil leakage from neighboring countries are important sources of pollution in this sea [3]. The Caspian, which is landlocked, has a less tolerant capacity than other seas, and the pollutants in it either undergo biochemical changes or remain in the sea for many years. Among the main pollutants are plastic, and nowadays plastics have taken over all the beaches [4].

The garbage collected on the beach accounts for about 80 percent of plastic waste and about 18 percent of the plastic waste found in the marine environment is in the fishing industry. These plastic wastes are transformed into fine particles due to the exposure to light, waves, wind currents and so on. Among particles found are initially large pieces of macro plastics and then fine particles of varying sizes between 0.999 to 5 mm, which are defined as micro-plastics [5, 6].

Macro plastics cause damage and death to marine birds, mammals, fish and reptiles because they are choked or trapped by swallowing macro plastics. Many species are forced to migrate to new habitats, and the more severe problem is the strangulation of the seabed through the prevention of gas exchange [7]. Micro-plastics are present throughout the water column and accumulate organic pollutants such as petroleum, PAHs[1], PCBs[2] and heavy metals such as lead, cadmium, etc., which enter the toxin into the food chain and intensify it to a higher nutritional level. The result is the extinction of many marine species [8].

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[1] Polycyclic aromatic hydrocarbons
[2] Polychlorinat biphenyls

Due to the adverse effects of micro-plastics on marine ecosystems, the aim of this project is to investigate the distribution of micro-plastics in sediments of the southern coast of the Caspian Sea.

2.Materials and methods

In this study, soil samples were taken from the coastline in Gilan province, south of the Caspian Sea in four different seasons of 2019. Three main strategies for micro-plastic sampling are identified. These three strategies are: selective sampling, mass sampling, and reduced volume [9]. Sedimentary samples are taken from the top of the tidal line on sandy beaches. There are four main steps for processing samples, namely density separation, filtration, screening and visual sorting. In this method, shape, type, stage of degradation and color of micro-plastics are considered as criteria for their identification [10].

In this study, the samples are first passed through a 10 mesh sieve because the aim of the present study is to evaluate micro-plastics. These samples were studied under an optical microscope. The number of micro-plastic parts observed per 100 grams of sample for each sampling station is specified. A quanta 250 scanning electron microscope was used to study the number of micro-plastics in the soil. Figure 1 shows examples of microscopic images obtained. The observed micro-plastic parts are in the form of fragments, fibers, foams and films.

After identifying the number of micro-plastics in the samples, the samples were washed with water and without any external force. The micro-plastics that floated in the water were identified as light micro-plastics. The remaining micro-plastics in the soil were identified as heavy micro-plastics. After determining the amount of pollutants in each season, we need to identify the type of pollutants. This means we need to know the exact types of plastic in each part. TGA-DSC analysis was used for this purpose. FTIR imaging was used to confirm the TGA-DSC results and to obtain the exact values of each type of micro-plastic.

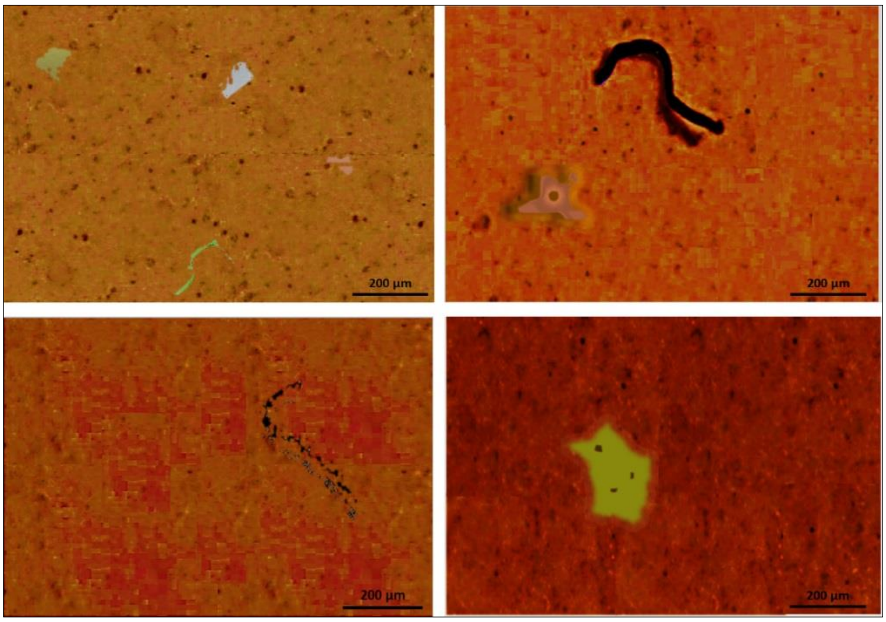

Figure 1. Optical microscope image of typical micro-plastic particles with different shapes

To study micro-plastic identification and quantification, a Fourier Transform Infrared (FTIR) imaging system was used which is comprised of an Agilent Cary 620 FTIR microscope coupled to an Agilent Cary 670 FTIR spectrometer. A TGA-DSC from Netzsch was used that was equipped with a Pt/Rh crucible with lead. The samples were heated from 25 to 600 °C in a streaming nitrogen atmosphere to suppress oxidation.

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3.Results and discussions

According to the results of microscopic studies, the number of micro-plastic particles per 100 grams of sample for 15 sampling stations and during four seasons is shown in Figure 2. The results show that the highest amount of micro-plastic contamination was in the summer and then autumn and the lowest was in the winter. The samples were then washed with water. Contaminants that floated in water during a simple wash process were labeled as light micro-plastics. The remaining micro-plastics were considered heavy micro-plastics because they did not float in water [11].

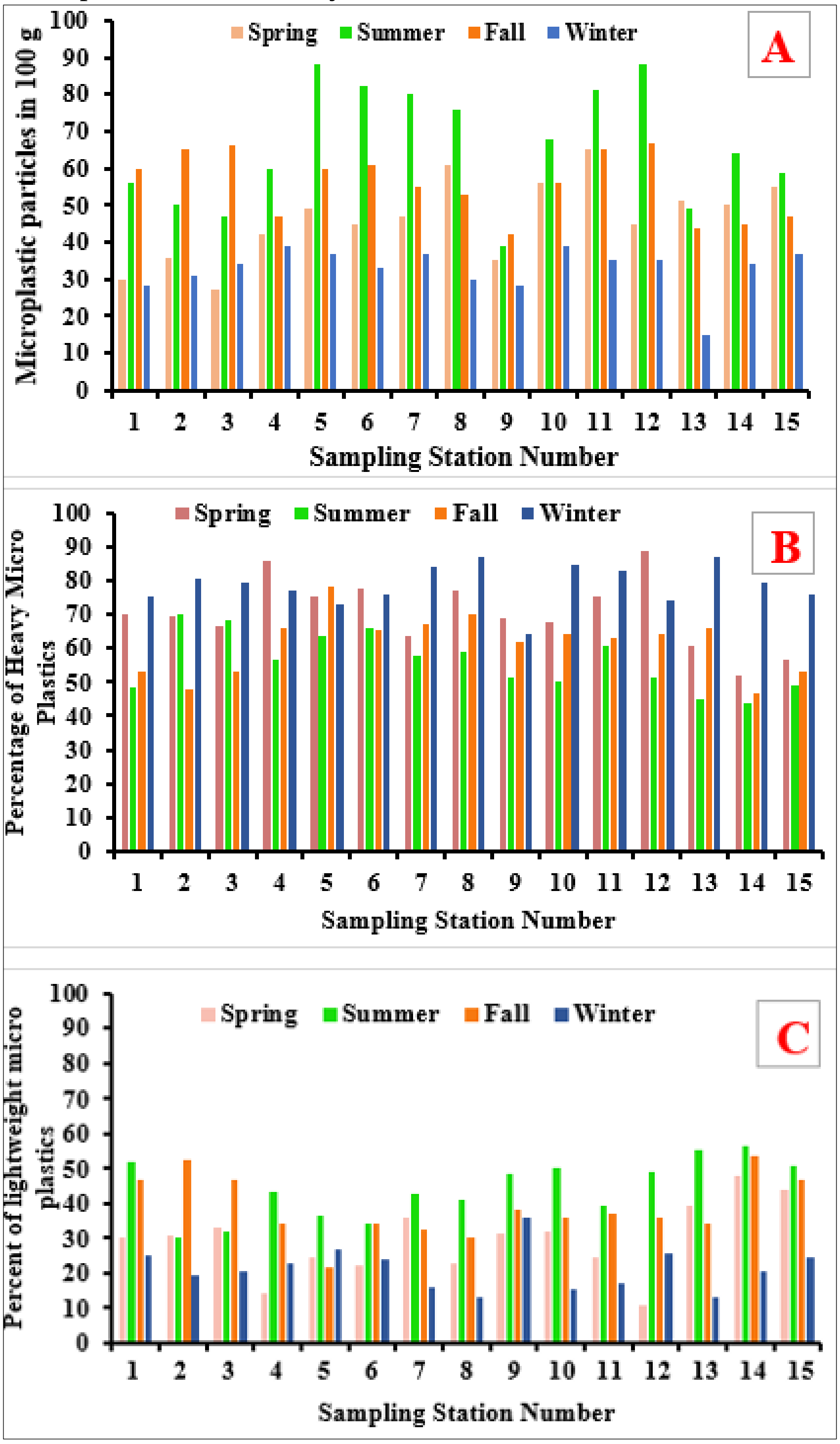

Figure 2. For different seasons: A. Number of micro-plastic per 100g of sample, B. Percentage of heavy micro-plastics, C. Percentage of light micro-plastics

As diagrams b and c in Figure. 2 show, the highest percentage of micro-plastics in all seasons is heavy plastic. However, there is a significant difference in the percentage of light and heavy micro-plastics in the springs and winter. In these two seasons, heavy micro-plastics are much more than light micro-plastics. There is a similar trend in the summers and autumn, but to a lesser extent. Table 1 provides a better understanding of these differences.

Table 1. Average percentage of heavy and light micro plastics from sampling points

	Spring	Summer	Autumn	Winter
Percentage of heavy micro-plastics	70.4	56	61.3	78.6
Percentage of lightweight micro-plastics	29.6	44	38.7	21.4

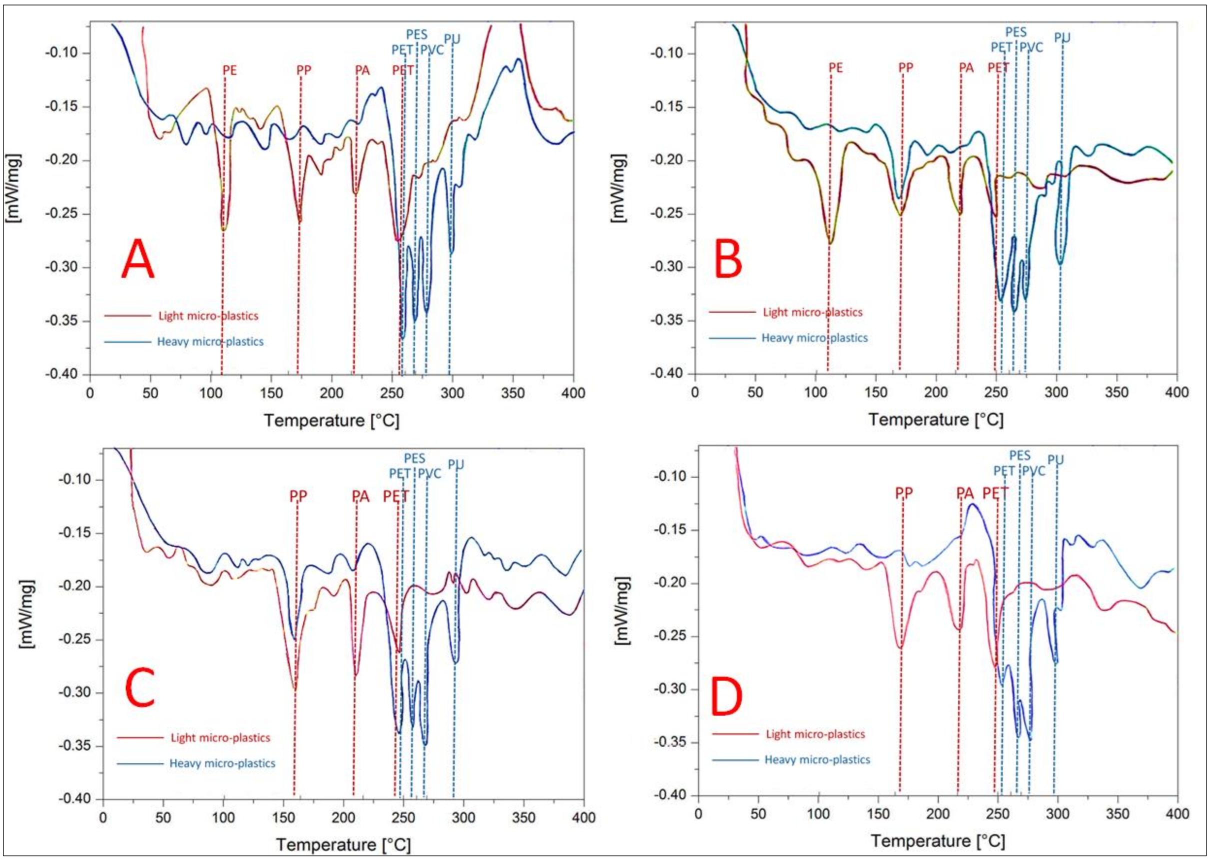

Figure 3. TGA-DSC analysis charts for light and heavy micro-plastic samples
A. Spring, B. Summer, C. Autumn and D. Winter

One way to more accurately identify micro-plastics is by implementing the TGA-DSC test [12]. According to the results obtained in the TGA-DSC test for light and heavy micro-plastic samples in each season of the year presented in Figure 3, the composition of the micro-plastic is shown in Table 2.

These results only confirm the correct separation of light and heavy micro-plastics in the single-step washing process and contain an important point. There is no PE in lightweight winter samples. This means that some pollutants have been removed in the winters, and based on the results of Table 1, it can be seen that there are many changes in the amount of pollutants in different seasons. We need to look at these changes quantitatively and with precision, so we use the FTIR imaging to better understand these changes over the seasons [13].

Table 2. TGA-DSC test of micro-plastic samples in each season

Season	Heavy micro-plastics	Light micro-plastics
Spring	PET[3], PES[4], PVC[5], PU[6]	PE[7], PA[8], PET, PP[9]
Summer	PET, PES, PVC, PU	PE, PA, PET, PP
Autumn	PET, PES, PVC, PU	PE, PA, PET, PP
Winter	PET, PES, PVC, PU	PA, PET, PP

For this reason, the FTIR imaging was performed to more accurately determine the types of micro-plastics in different samples. Performing this analysis along with TGA-DSC analysis can provide more verified and reliable results.

Since the results of the analysis included different types of plastics in the sample and the expression of all its types was very complicated and misleading, in this study we have included only the samples whose value is more than one percent. The results of this study are shown in Figure 4 and Table 2.

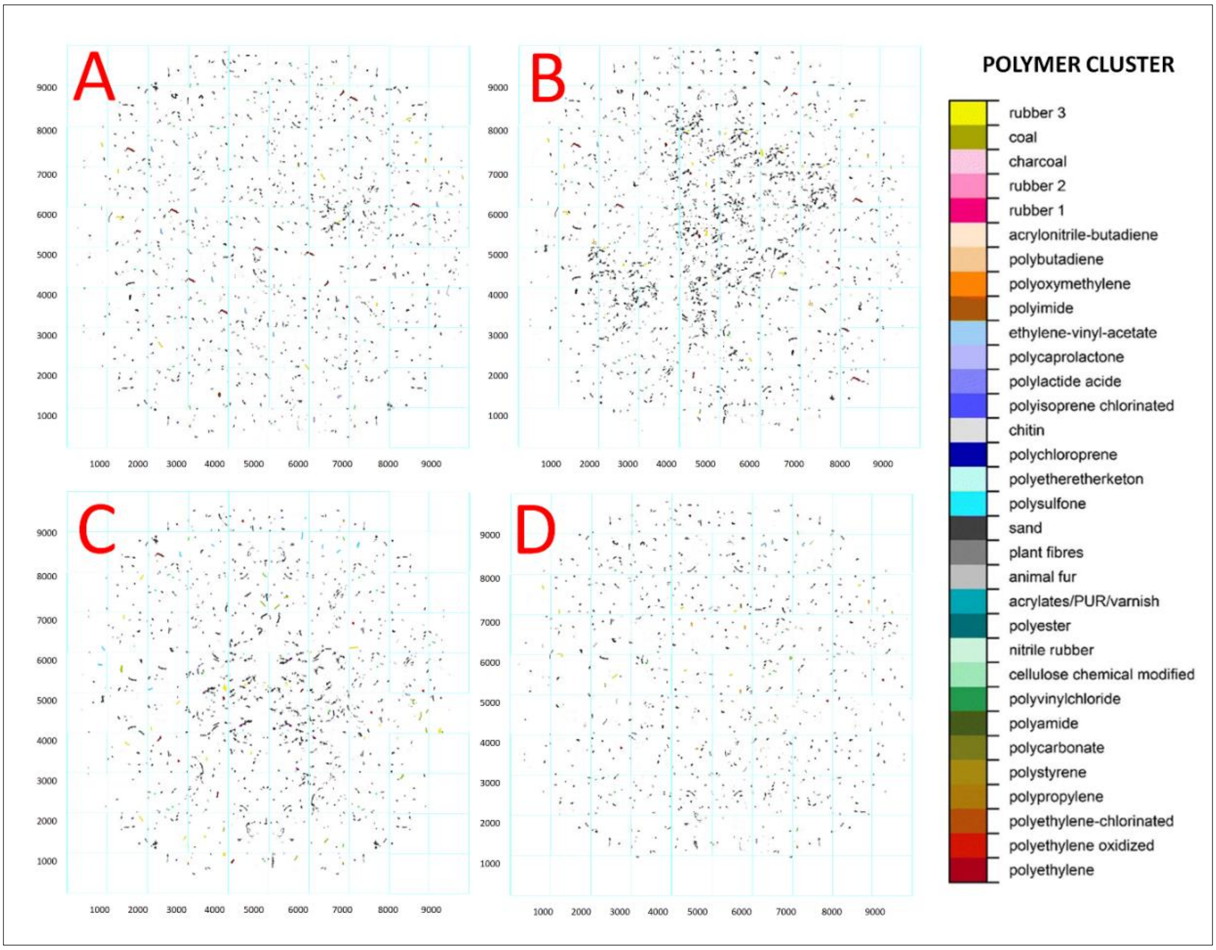

Figure 4. FTIR imaging for micro-plastic samples A. Spring, B. Summer, C. Autumn and D. Winter

[3] Polyethylene terephthalate
[4] Polyethersulfone
[5] Polyvinyl chloride
[6] Polyurethane
[7] Polyethylene
[8] Polyamide/Nylon
[9] Polypropylene

Table 3. FTIR imaging results of micro-plastic samples in each season

Season / MP type	Spring	Summer	Autumn	Winter
PE	6.12	10.14	7.44	3.19
PP	7.16	9.15	9.95	2.66
PA	4.43	9.44	9.12	5.12
PET	13.67	7.50	8.89	6.25
PU	11.94	7.18	8.21	16.17
PES	15.02	6.45	12.01	19.12
PVC	19.16	7.03	14.10	21.37
POM[10]	1.11	1.03	1.01	2.01
PL[11]	1.06	2.36	2.03	1.09
PS[12]	1.12	1.72	1.09	1.43
EP[13]	1.40	1.46	1.23	1.28
Total	**82.19**	**70.26**	**75.08**	**79.69**

4.Conclusions

Various studies have shown that the amounts of micro-plastics in sediments, coastal sand and soil are completely different in different places. This study concluded that the amount of micro-plastics also varies at different times.

The results of this study showed that various factors such as the change of seasons, precipitation and type of micro-plastics affect the temporal variation of the frequency of micro-plastics.

In the winter and spring, as the volume of precipitation increases, it washes out light micro-plastics from the soil, and takes them to the sea. As a result, the percentage of light micro-plastics in these two seasons decreases, and what remain in the soil are heavy micro-plastics. But in the autumn and summer, the difference less significant.

In the spring, the highest levels of pollutants are PVC, PES, PET and PU, respectively. In the summer, the values of PE, PP, PA, PAT, PU and PVC are in a relatively equal range. In the autumn, as in the summer, most pollutants are relatively even. In the winter, most of the pollutants are PVC, PES, and PU.

Given that the levels of pollutants PE, PP, PA, and PET are less than other seasons in the winter and to some extent in the spring, we conclude that these pollutants are washed away by the rains in these seasons and are transferred to the sea.

If local authorities are looking for a means to solve the problem of micro-plastics in a given area, the contaminants of PE, PP, PPA, and PET should be removed from the environment before they can be modified by physical and chemical processes. This means that these contaminants are still present when they are still macro-plastic. Therefore, it is important to identify the source of these pollutants.

Based on the experience gained from this study, we think that other factors such as soil organisms, sunlight, soil chemical composition, chemical composition of water, and wind rate affect micro-plastic changes in soil and these parameters need further investigation.

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[10] Polyoxymethylene
[11] Plastic lumber
[12] Polystyrene
[13] Ethylene propylene

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Manuscript received: 23.11.2020