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Investigation of Microplastic Pollution in Sediments from the Port of Tripoli, Libya

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دراسة تلوث الرواسب باللدائن الدقيقة في ميناء طرابلس، ليبيا

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Abstract:
The heightened concern for microplastics in the environment and coastal regions drives investigations into their presence in the environment, including seacoasts, to minimize plastic leakage into the ecosystem. This study was conducted in the west of Libya to identify the microplastics in different locations near the Port of Tripoli on the Mediterranean Sea. It employed GIS to determine the study areas and Fourier Transform Infrared (FTIR) spectroscopy to analyze and identify the microplastics. The study collected samples from 15 points of a selected site (Section A) on the coastline of the Port of Tripoli between May 2022 and May 2023 and recorded the highest average MP (polymer)/area. The FTIR analysis showed that the polymers in the samples from Section A consist of ten types of microplastics, primarily polyethylene (40%), polypropylene (26%), and polystyrene (13%). This study is the first to determine their presence at the Port of Tripoli in the west of Libya. Analysis of the samples from Section A demonstrated that the adopted techniques efficiently identified the Microplastic contamination.

Keywords: Plastic pollution, Port of Tripoli, Microplastics, GIS, FTIR, Database.

الملخص:
تُثير الزيادة الملحوظة في الاهتمام بالجسيمات البلاستيكية الدقيقة (Microplastics) في البيئة والمناطق الساحلية اهتمامًا متزايدًا بدراسة وجودها وانتشارها في البيئات المختلفة، بما في ذلك السواحل البحرية، بهدف الحد من تسرب المواد البلاستيكية إلى النظام البيئي. أُجريت هذه الدراسة في الجزء الغربي من ليبيا بهدف تحديد وجود الجسيمات البلاستيكية الدقيقة في مواقع مختلفة بالقرب من ميناء طرابلس على ساحل البحر الأبيض المتوسط. واعتمدت الدراسة على نظم المعلومات الجغرافية (GIS) لتحديد مناطق الدراسة، وعلى مطيافية الأشعة تحت الحمراء بتحويل فورييه (FTIR) لتحليل الجسيمات البلاستيكية الدقيقة والتعرّف عليها. جُمعت العينات من 15 نقطة ضمن موقع مختار) القطاع (A على الخط

الساحلي لميناء طرابلس، وذلك خلال الفترة الممتدة من مايو 2022 إلى مايو 2023، حيث سُجل أعلى متوسط لعدد الجسيمات البلاستيكية الدقيقة (MP) من حيث نوع البوليمر/المساحة. وأظهرت تحاليل FTIR أن البوليمرات الموجودة في عينات القطاع A تتكون من عشرة أنواع من المواد البلاستيكية الدقيقة، وكان أكثرها شيوعًا البولي إيثيلين (40%)، يليه البولي بروبيلين (26%) والبولي ستايرين (13%). وتُعد هذه الدراسة الأولى من نوعها التي تحدد وجود الجسيمات البلاستيكية الدقيقة في ميناء طرابلس غرب ليبيا. كما أظهر تحليل عينات القطاع A أن التقنيات المعتمدة في هذه الدراسة تتمتع بكفاءة عالية في تحديد تلوث البيئة بالجسيمات البلاستيكية الدقيقة.

الكلمات المفتاحية: التلوث البلاستيكي، طرابلس، الجسيمات البلاستيكية، الدقيقة، نظم المعلومات الجغرافية(GIS) ، مطيافية الأشعة تحت الحمراء، قاعدة البيانات.

Introduction:

Microplastics (MPs) are, plastic wastes less than 5 mm in size (Andrady, 2011). They are recognized as environmental pollutants and have garnered substantial interest because of their harmful impacts on humans and other living organisms. Depending on their origin, MPs can be classified as primary or secondary. The wide distribution of marine litter, particularly MPs, is detrimental to the environment and human health, although their most severe impacts are on aquatic habitats and coastal areas. Carpenter et al. (1972) were the first to publish an article warning about the presence of plastic pellets on the surface of the North Atlantic Ocean. Since then, researchers across the globe have become increasingly concerned about the detrimental impacts of plastic pollution (Llorca et al., 2020).

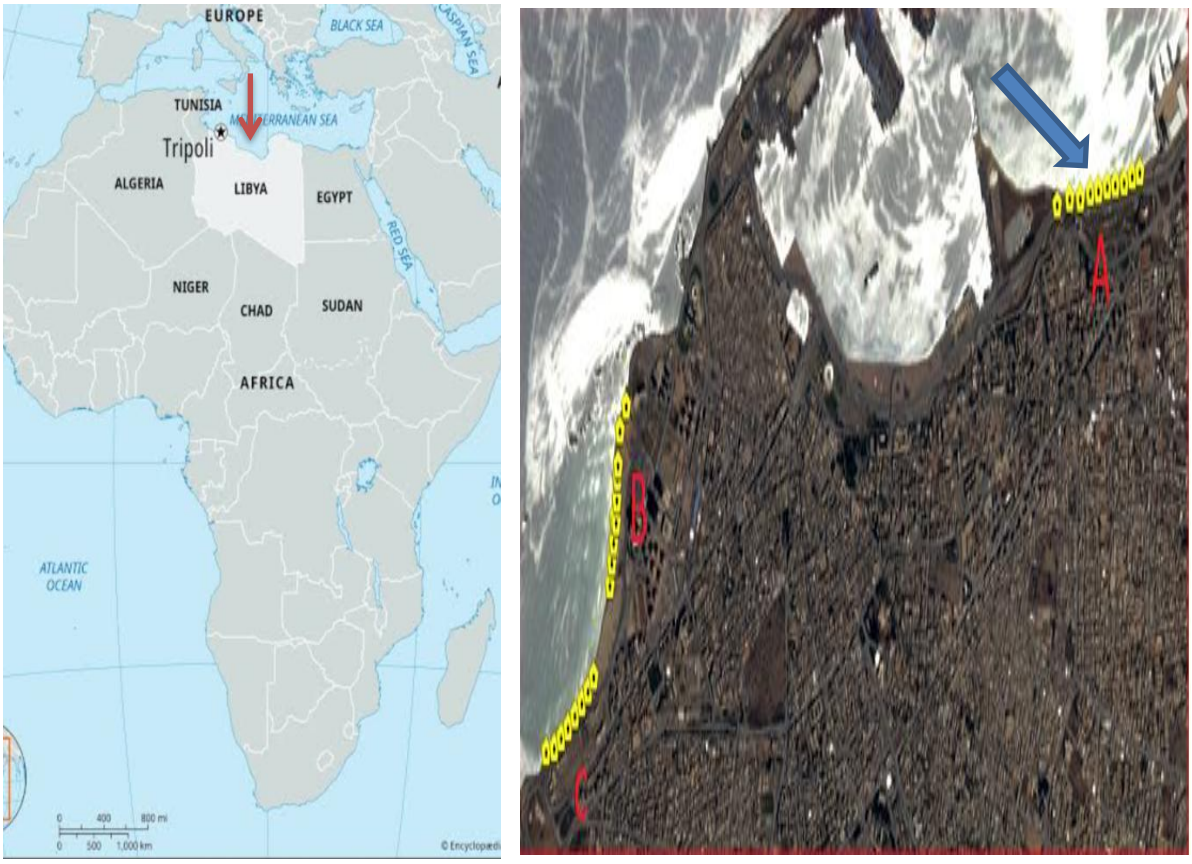
The pollution in the Mediterranean Sea has worsened with the increase in oil production and sea transport. Drilling and oil rig operations, pipeline leaks, and natural oil leakage from neighboring countries are also the primary contributors to the pollution in the Mediterranean Sea (Shirneshan et al., 2017). The primary beach pollutant is ubiquitous plastic litter (Ghayebzadeh et al., 2020). The fishing industry contributes to the garbage accumulation on beaches, approximately 80% of which is plastic waste, and about 18 percent of waste in the aquatic environment is plastic debris (Abadi et al., 2019). Sunlight, waves, wind, currents, and other factors transform these wastes into particles.

Microplastics are large plastic pieces, typically more than 5 mm, and microplastics, or fine particles, range from 0.999 to 5 mm in size (Jafari, N., 2010; Nelms et al., 2018). Microplastics are widespread in water due to effects of chemical, physical, and environmental factors, and organic pollutants, such as petroleum, PAHs1, and PCBs2, and heavy metals, such as lead and cadmium, enter the food chain and accumulate to high levels and contribute to the extinction of many marine species (Mendoza et al., 2015). Previous research focused on the deposition of MPs from natural waters into the coastal areas because they are more prone to mechanical and, to an extent, UV degradation in sand than in water (Corcoran et al., 2009).

Continuous exposure to the breakdown pathways results in higher quantities of smaller MP particles, which is critical since research has demonstrated that MPs increase in toxicity as their size decreases (Hwang et al., 2020). This study collected samples from the beach sediment the Port of Tripoli and subjected them to FTIR analysis to identify the microplastics in the samples. The Fourier transform infrared spectroscopy (FTIR) obtains the infrared spectrum of the absorption or emission of a solid, liquid, or gas and simultaneously collects high-spectral resolution data over a wide spectral range (Claudia et al., 2023; Verleye et al., 2001). This study conducted the FTIR analysis at a spectra range of650-4,000cm^{-1} and compared the results with the reference characteristic wave numbers provided by the Easy Identification of Plastics and Rubbers (CBD, 2012). The results provided insight into the MP pollution at the port and contributed to facilitating its monitoring.

Materials and Methods:

Study Area:



a) b)

Figure (1): (a): Location of the Port of Tripoli.
(b): Section A at the Port of Tripoli (latitude N 32◦ 54◦ 10◦.19 and longitude 13◦ 11◦ 21◦.60 E).

The study area comprises three sections, A, B, and C, and Figure 1 shows the GIS image for the area. The study area extends approximately five kilometers to the right and left of the port basin, and ten samples were collected from each section. This paper presents the result of the FTIR analysis to identify the type and amount of microplastics found in Section A.

Sampling:

The sample collection is as follows:

1. The study location was divided into squares based on the MSFD: European Commission's Marine Strategy.
2. Each square is 50x50cm. The sand collection and sifting process took between one to two hours.
3. The seawater from one square was filtered through a 100-300 micrometer plastic net into a clean bucket and used to wash the sand.
4. The MSFD guideline recommends collecting the sand at a depth of 5 cm, measured using a metal ruler.
5. The sand was sifted to separate all elements between 1 - 5 mm in size.
6. The samples were transferred to the laboratory and put under a microscope to identify the Microplastic particles ranging from 1 to 5 mm. They were then kept in a small glass container and later subjected to FTIR analysis (Figure 2) to identify the types of polymers.

Chemical Analysis:

FTIR technology provides an accepted and reliable laboratory method without any restrictions. The sample preparation and measurements for the investigation are time-consuming (one day for sample

preparation and four to eight hours for measurements) without severe constraints. Depending on the analytical questions, the technique is adaptable to diverse environmental materials and particle sizes (Stuart B. H., 2004). The spectra of the samples were compared with those of the reference plastics, and the identification of the microplastics was based on their similarity to the library references.

Sample Analysis:

The instrumental process is as follows:

1. The infrared energy emitted from a glowing black-body source passes through an aperture, which controls the amount of energy reaching the sample (and, ultimately, the detector).
2. The beam enters the interferometer, where the spectral encoding takes place, and the resulting interferogram signal then exits the interferometer.
3. The beam enters the sample compartment, where it is transmitted through or reflected off the sample surface, depending on the type of analysis. The sample absorbed the energy frequencies that correspond with its molecular composition.
4. The beam passes to the detector designed to measure the unique interferogram signal for the final measurement.
5. The measured signal is digitized and sent to the computer for the Fourier transformation, which generates the final infrared spectrum for the user to interpret and perform further manipulation, if any. Figure 2 shows the sample analysis process.

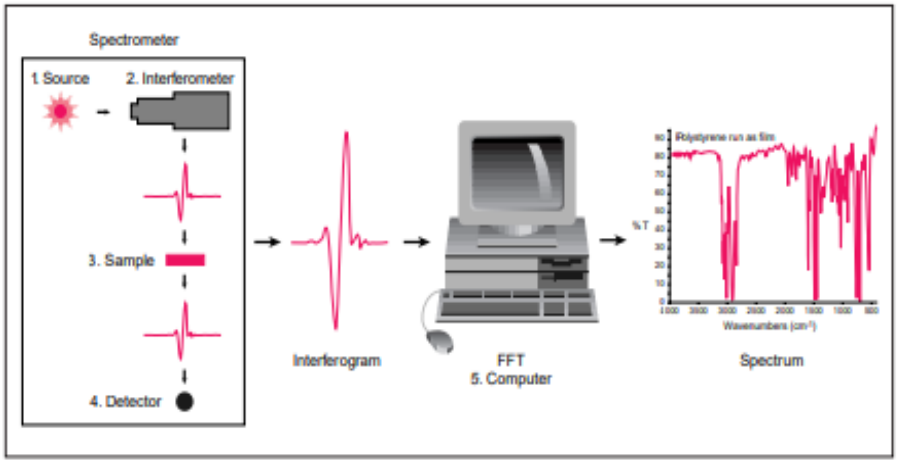


Figure (2): Sample Analysis Process.

Results:

The FTIR results (Table 1) show that most MPs (40%) in Section A (ten samples from 15 points) are polyethylene (PE), which is present in six of the 15 points (A1 blue, A1 white, A3 white, A5 white Sample1, A5 white Sample2, and A7 white). The Poly (ethylene) – low-density (PELD) from two sample points (A4 blue and A8 blue) make up 13.33% of the sample. Figure (3 presents section A (latitude N 32° 54° 10°.19 and longitude 13° 11° 21°.60 E).

Figure (3): Section A (latitude N 32° 54° 10°.19 and longitude 13° 11° 21°.60 E).

Polypropylene (PP) is present in four sample points, making up 26.66%of the sample. Poly(styrene), atactic comprises13.33%of the sample, and styrene-butadiene block polymer (SB)is present in one sample point and makes up 6.66%of the sample. Each sample from the ten points of Section A is one hundred meters from one another. The order of the compounds is PE>PP>PS and PELD > SB.

Table (1): Comparison of the microplastics in Section A, comprising 15 points, to the library reference.

Point	Index	Sample	Match %	Compound name	Library reference
1	625	A1 blue	86.96	Polyethylene	HR Nicolet Sampler Library
2	625	A1 white	62.55	Polyethylene	HR Nicolet Sampler Library
3	41	A2 white	68.49	Poly(propylene), atactic	Hummel Polymer Sample Library
4	46	A3 sky color	91.52	Poly(styrene), atactic	Hummel Polymer Sample Library
5	625	A3 white	76.14%	Polyethylene	HR Nicolet Sampler Library
6	95	A4 blue	85.69%	poly(ethylene), low density	Aldrich Condensed Phase Sample Library
7	625	A5 white Sample1	86.96	Polyethylene	HR Nicolet Sampler Library
8	625	A5 white Sample2	91.76	Polyethylene	HR Nicolet Sampler Library
9	41	A6 blue	69.25	poly(propylene), atactic	Hummel Polymer Sample Library
10	41	A6 green	77.8	Poly(propylene), atactic	Hummel Polymer Sample Library
11	625	A7 white	91.47	Polyethylene	HR Nicolet Sampler Library
12	95	A8 blue	76.1	Poly(ethylene), low density	Aldrich Condensed Phase Sample Library
13	41	A8 white	76.32	Poly(propylene), atactic	Hummel Polymer Sample Library
14	734	A9 red	72.37	Styrene butadiene block polymer	HR Nicolet Sampler Library
15	46	A10 white	66.89	Poly(styrene), atactic	Hummel Polymer Sample Library

Table (2): Percentage of the primary microplastic compounds in Section A.

Compound name	No. of sampling points	Percentage %
Polyethylene (PE)	6	40%
Polypropylene (PP)	4	26.66%
Poly(ethylene), low density (PELD)	2	13.33%
Poly (Styrene)(PS)	2	13.33%
Styrene butadiene block Polymer (SB)	1	6.66%

Table 2 shows the primary compounds in the ten samples distributed in the fifteen points of Section A. Polyethylene was the most prevalent in this area (six points), followed by Propylene (four points) and Polystyrene (two points). Figure 4 shows the chemical structure of the three primary compounds.

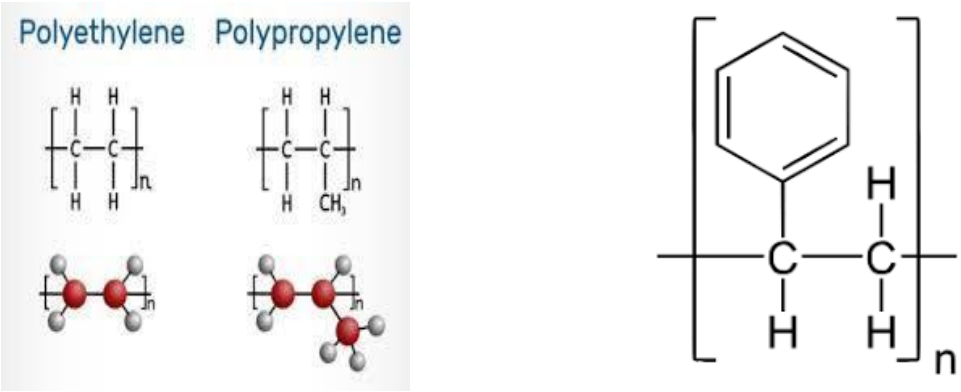


Figure (4): Single-bond compounds and cyclic polystyrene.

The Microplastic Compounds Identified through FTIR Analysis.

Polyethylene (PE):

Polyethylene (PE)is present at six (40%) of the fifteen points (Table 2). Figures 5, 6,7,8,9, and 10show the peaks indicating that the PE region is between wave numbers 3,000 to 4,000.

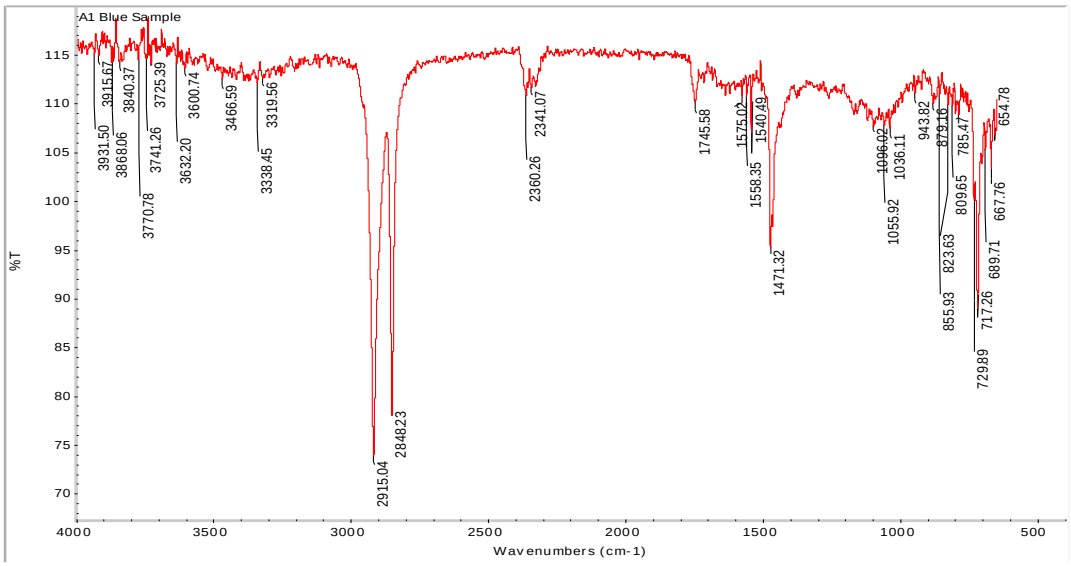


Figure (5): The A1 blue sample contains 85.85% Polyethylene (PE).

The FTIR spectroscopy (Table1 and Figure 5) shows an 85.85% possibility of the A1 blue sample having the spectra for Polyethylene microplastic compared to the PE library spectrum. The peaks are between 654 and 3,931 cm^{-1}.

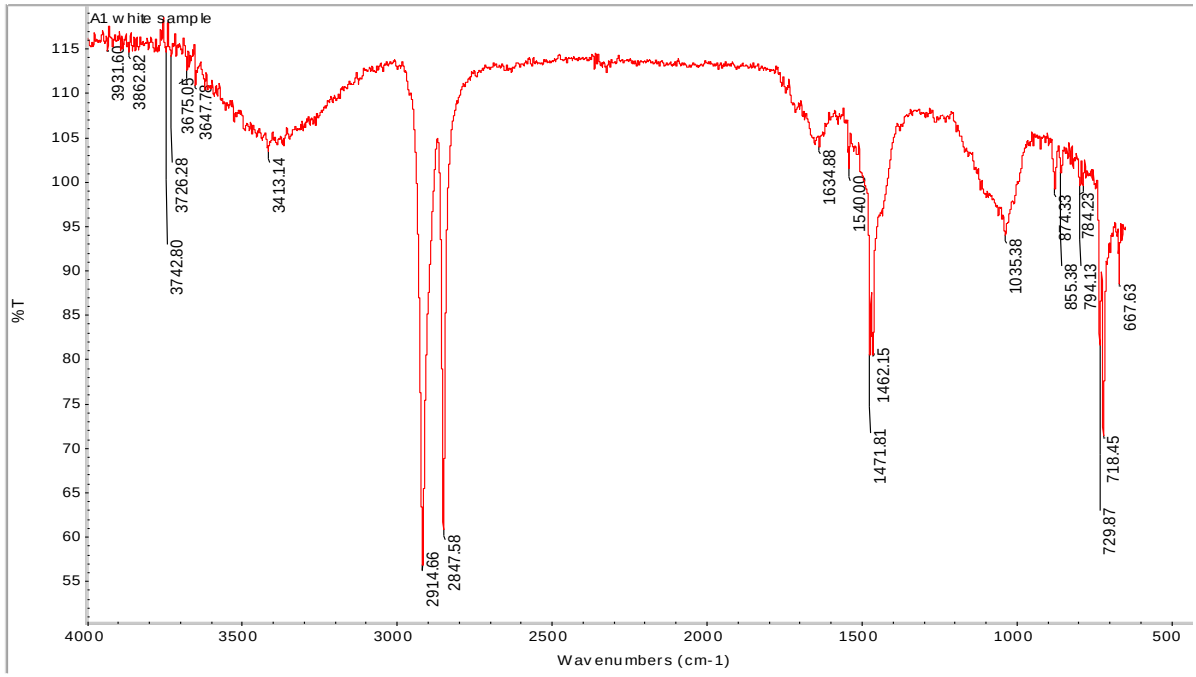


Figure (6): The A1 white sample contains 86.96 % Polyethylene.

The FTIR spectroscopy (Table1 and Figure 6) shows an 86.96 % possibility of the A1 white sample having the spectra for Polyethylene microplastic compared to the PE library spectrum. The peaks are between 667 and 3,931 cm^{-1}.

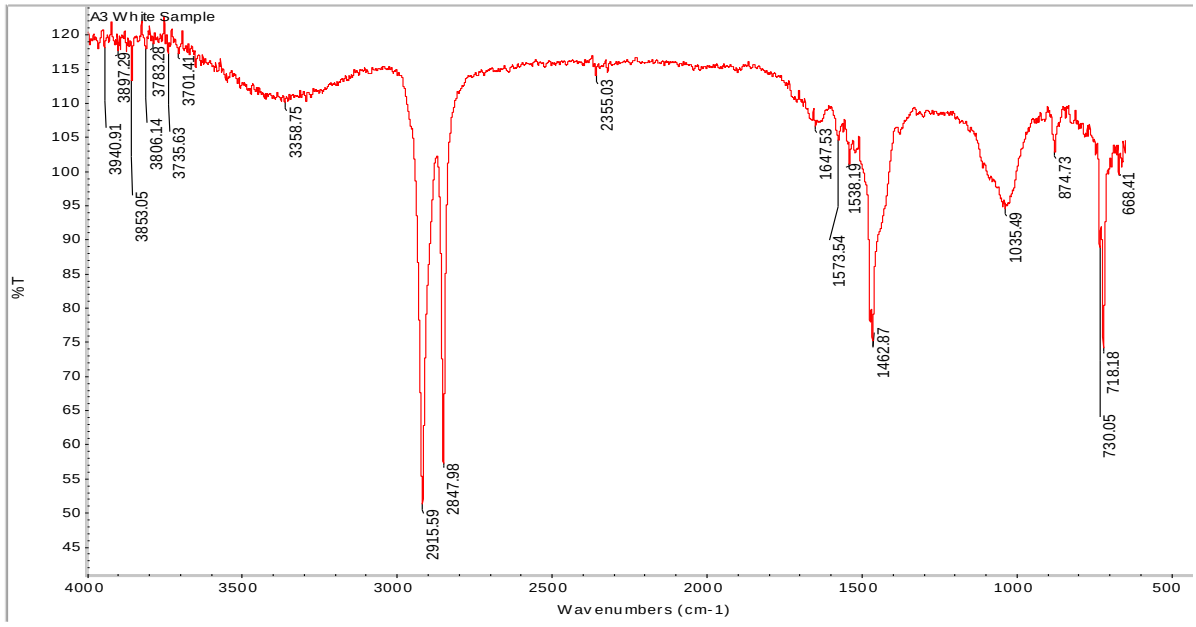


Figure (7): A3 White Sample contains 91.52 % Polyethylene.

The FTIR spectroscopy (Table1 and Figure 7) shows an 91.52 % possibility of the A3 white sample having the spectra for Polyethylene microplastic compared to the PE library spectrum. The peaks are between 668 and 3,940 cm^{-1}.

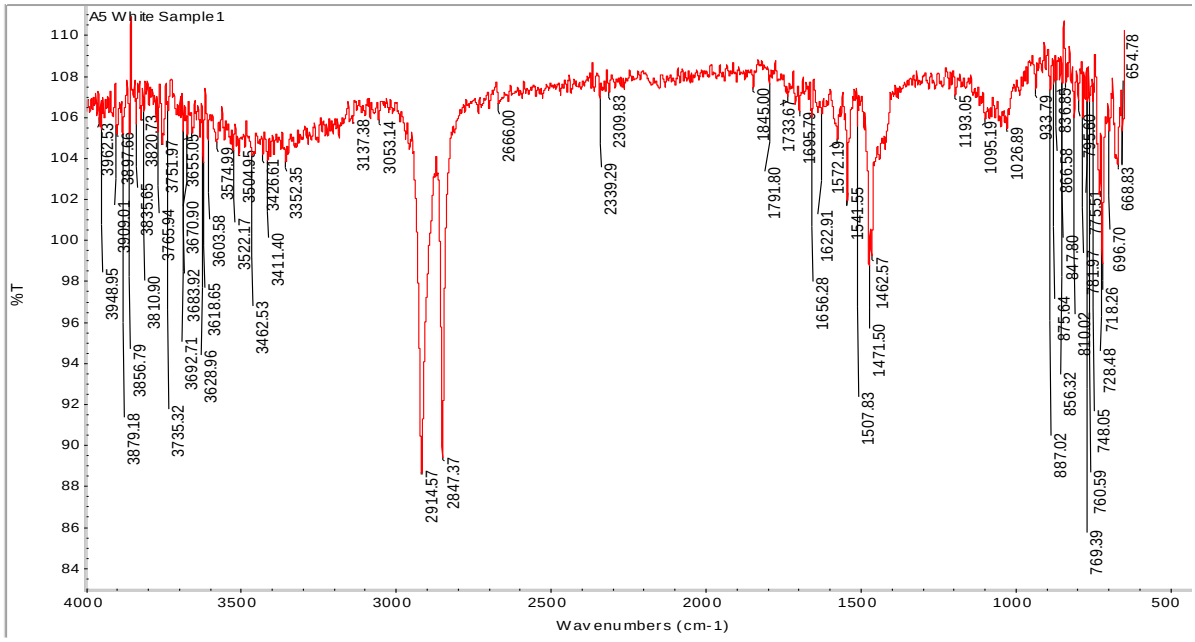


Figure (8): A5 White Sample1 contains 85.69% Polyethylene.

The FTIR spectroscopy (Table1 and Figure 8) shows an85.69% possibility for theA5 white Sample 1 having the spectra for Polyethylene microplastic compared to the PE library spectrum. The peaks are between 654 and 3,962 cm^{-1}.

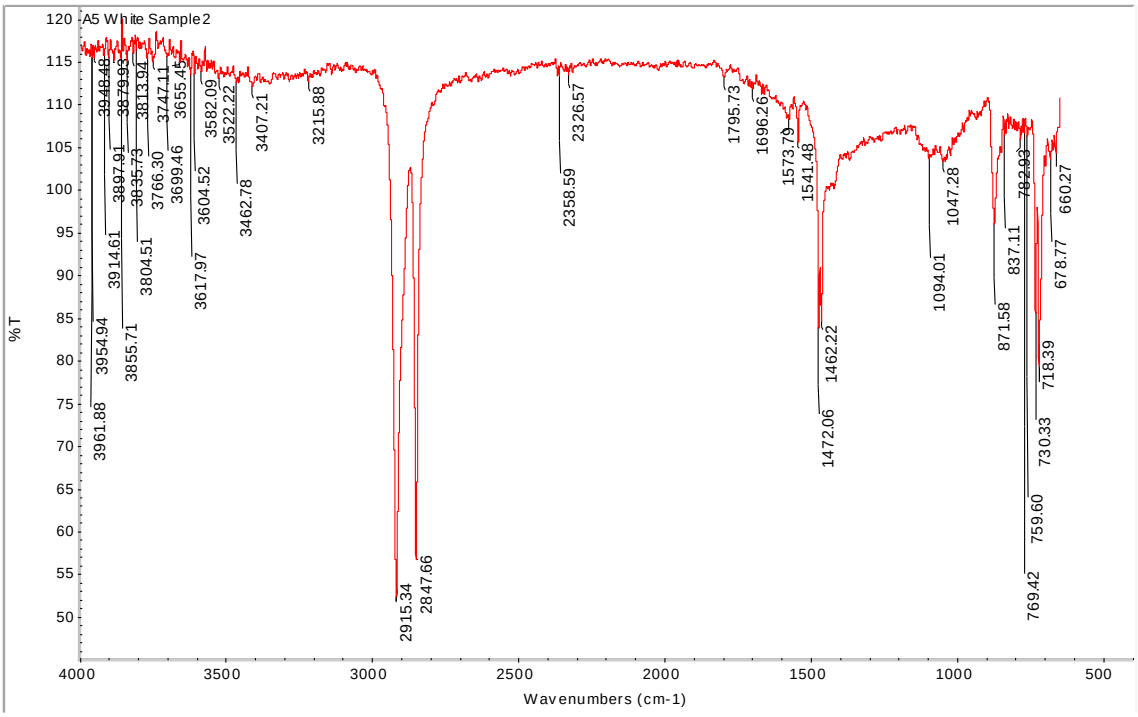


Figure (9): A5 White Sample2 contains 91.76% polyethylene.

The FTIR spectroscopy (Table1 and Figure 9) shows a 91.76% possibility for the A5 white Sample2 having the spectra for Polyethylene microplastic compared to the PE library spectrum. The peaks are between 660 and 3,961 cm^{-1}.

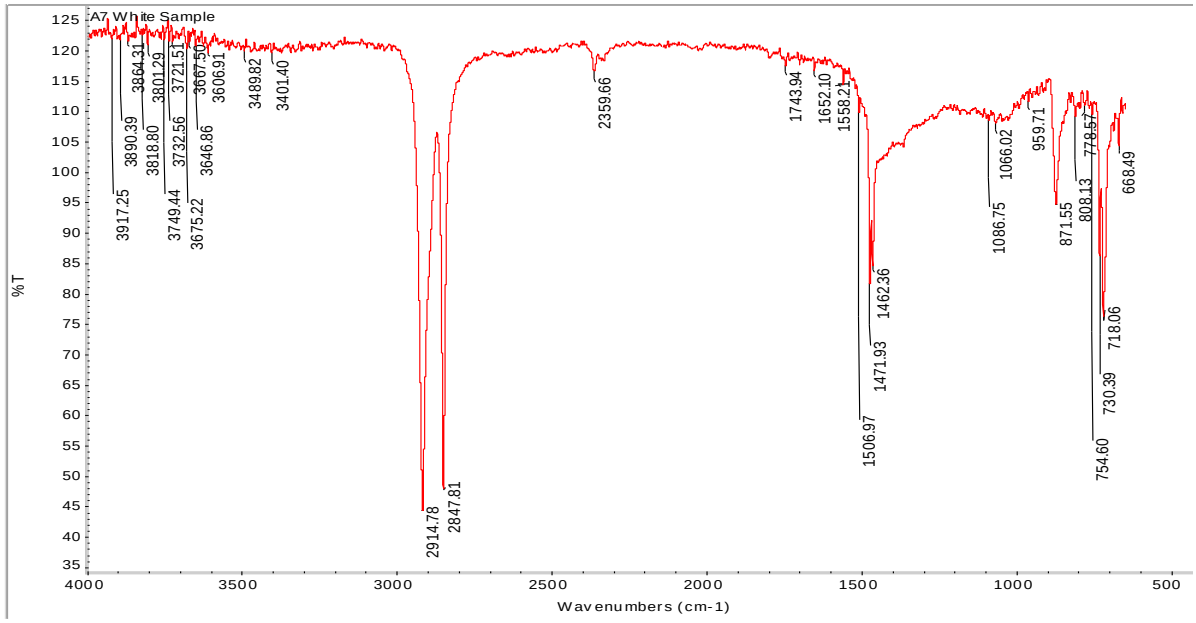


Figure (10): A7 White Sample contains 91.47% Polyethylene.

The FTIR spectroscopy (Table1 and Figure 10) shows an 91.47% possibility for the A7 white sample having the spectra for Polyethylene microplastic compared to the PE library spectrum. The peaks are between 668 and 3,917 cm^{-1}.

Polypropylene (PP):

Polypropylenes present at four points (26.66%) of the 15 points (Table2). Figures11, 12, 13, and 14 show the FTIR peaks for Polypropylene.

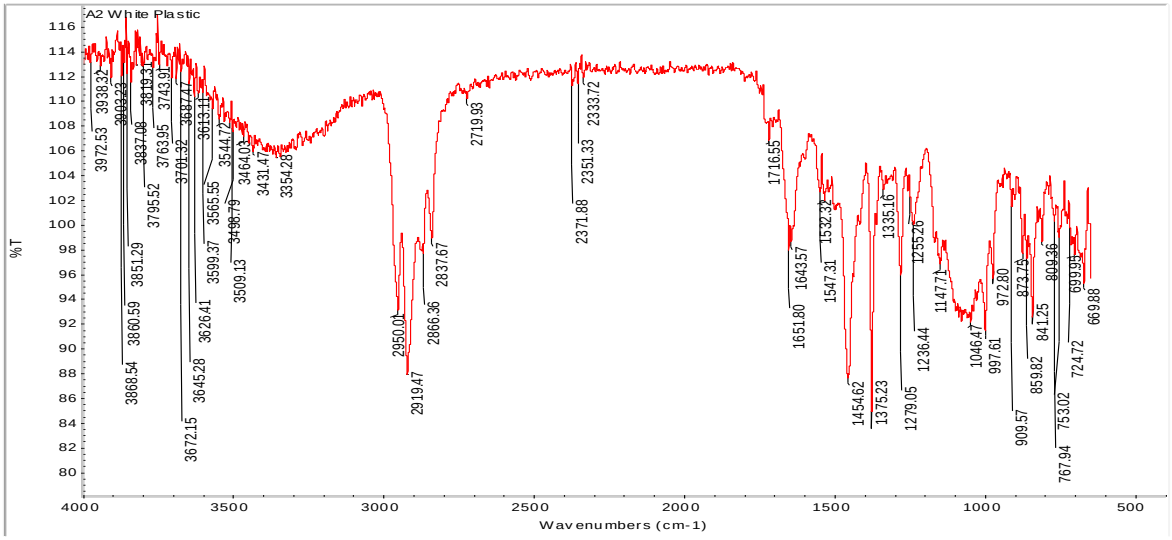


Figure (11): A2 white plastic contains 62.55 % Poly(propylene), atactic.

The FTIR spectroscopy (Table1 and Figure 11) shows a 62.55% possibility for the A2 white plastic sample having the spectra for Poly (Propylene), atactic microplastic compared to the Poly (Propylene), atactic library spectrum. The peaks are between 669 and 3,972cm^{-1}.

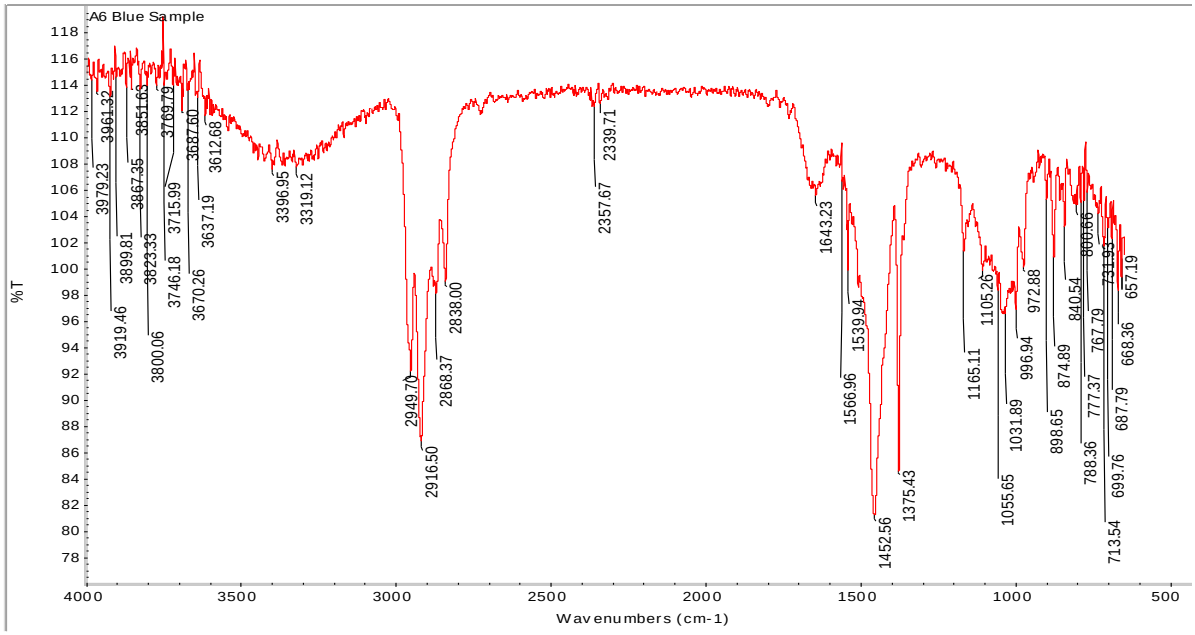


Figure (12): A6 blue sample contains 69.25% Poly (Propylene), Atactic.

The FTIR spectroscopy (Table1 and Figure 12) shows a 69.25% possibility for the A6 blue sample having the spectra for Poly (Propylene), atactic microplastic compared to the Poly (Propylene), atactic library spectrum. The peaks are between 657 and 3,979 cm^{-1}.

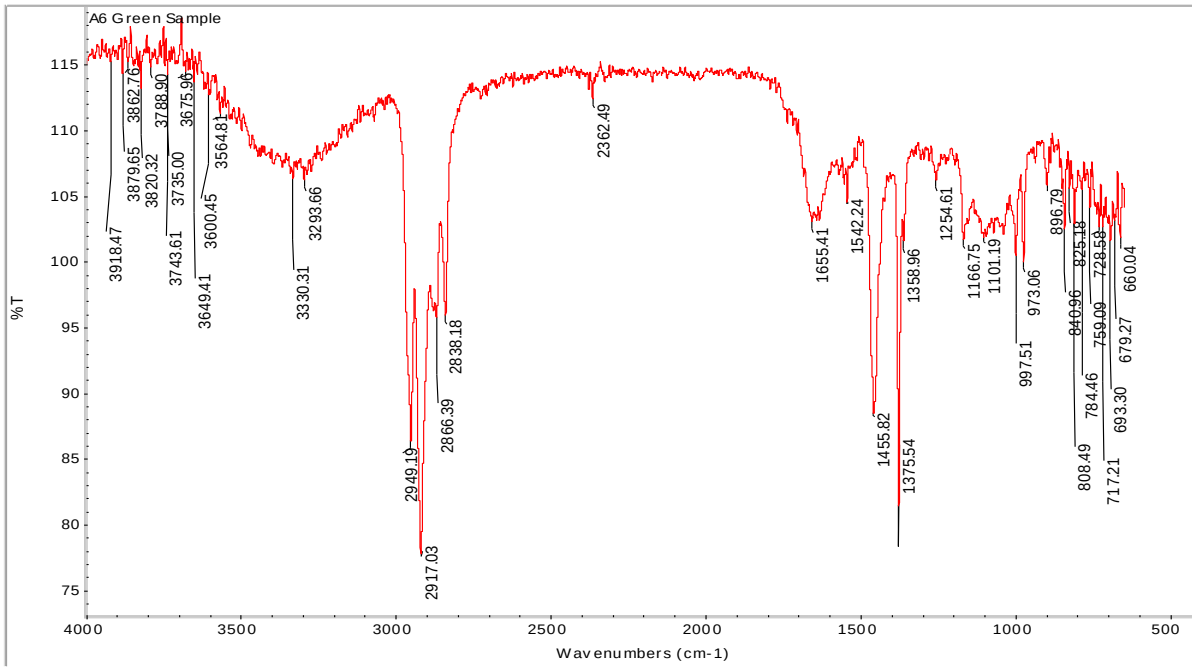


Figure (13): A6 Green Sample contains 77.8% Poly (Propylene), atactic.

The FTIR spectroscopy (Table1 and Figure 13) shows a 77.8% possibility for the A6 green sample having the spectra for Poly (Propylene), atactic microplastic compared to the Poly (Propylene), atactic library spectrum. The peaks are between 660 and 3,918 cm^{-1}.

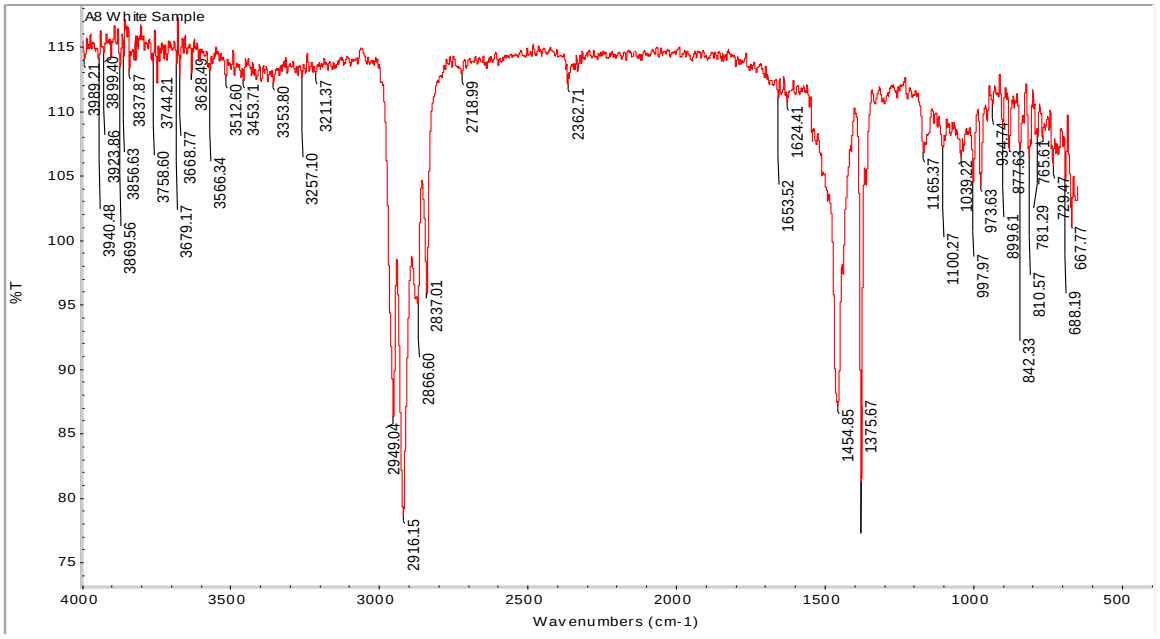


Figure (14): The A8 White Sample Contains 76.32% Poly (Propylene), Atactic.

The FTIR spectroscopy (Table1 and Figure 11) shows a 76.32% possibility for the A1blueplastic sample having the spectra for Poly (Propylene), atactic microplastic compared to the Poly (Propylene), atactic library spectrum. The peaks are between 667 and 3,989 cm^{-1}.

Poly (Styrene) (PS):

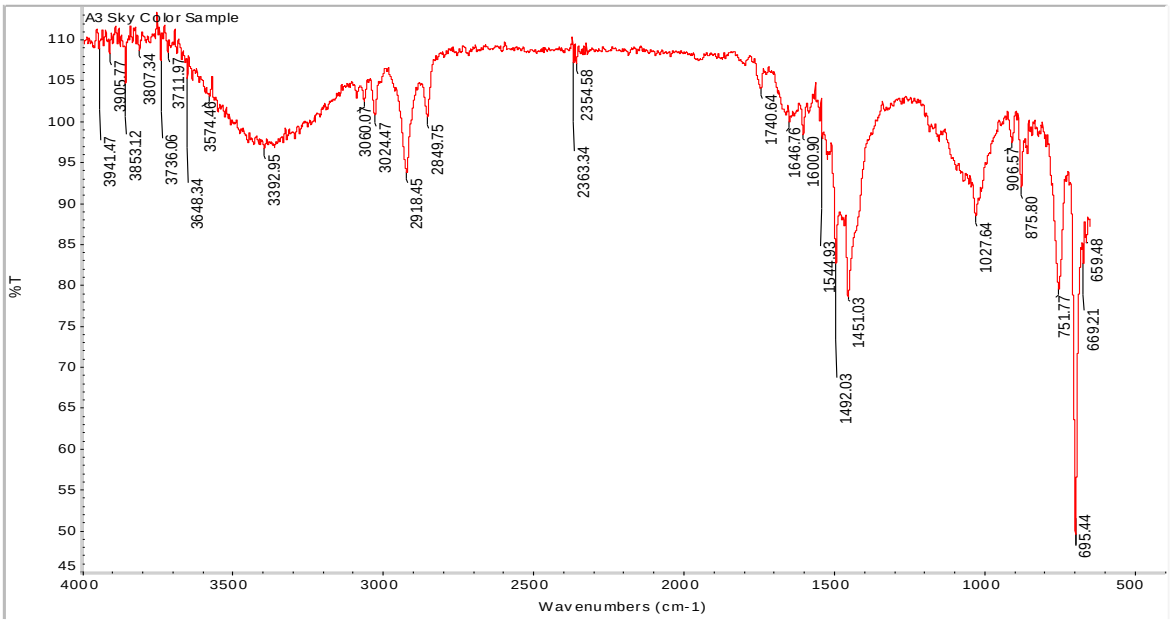


Figure (15): A3 Sky Color contains 68.49 % Poly (Styrene), Atactic.

The FTIR spectroscopy (Table1 and Figure 15) shows a 68.49% possibility for the A3 Sky Color sample having the spectra for Poly (Styrene), atactic microplastic compared to the Poly (Styrene), atactic library spectrum. The peaks are between 659 and 3,941 cm^{-1}.

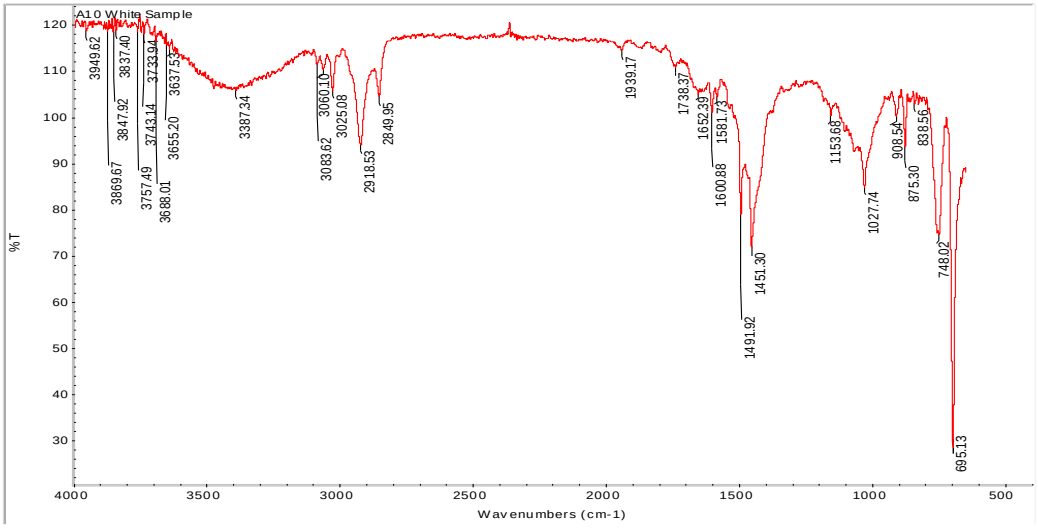


Figure (16): A10 White Sample contains 66.89%Poly (Styrene), Atactic.

The FTIR spectroscopy (Table1 and Figure 15) shows a 66.89% possibility for the A10 white sample having the spectra fo**r** Poly (Styrene), atactic microplastic compared to the Poly (Styrene), atactic library spectrum. The peaks are between695 and 3,949 cm^{-1}.

Poly (Ethylene), Low Density (PELD):

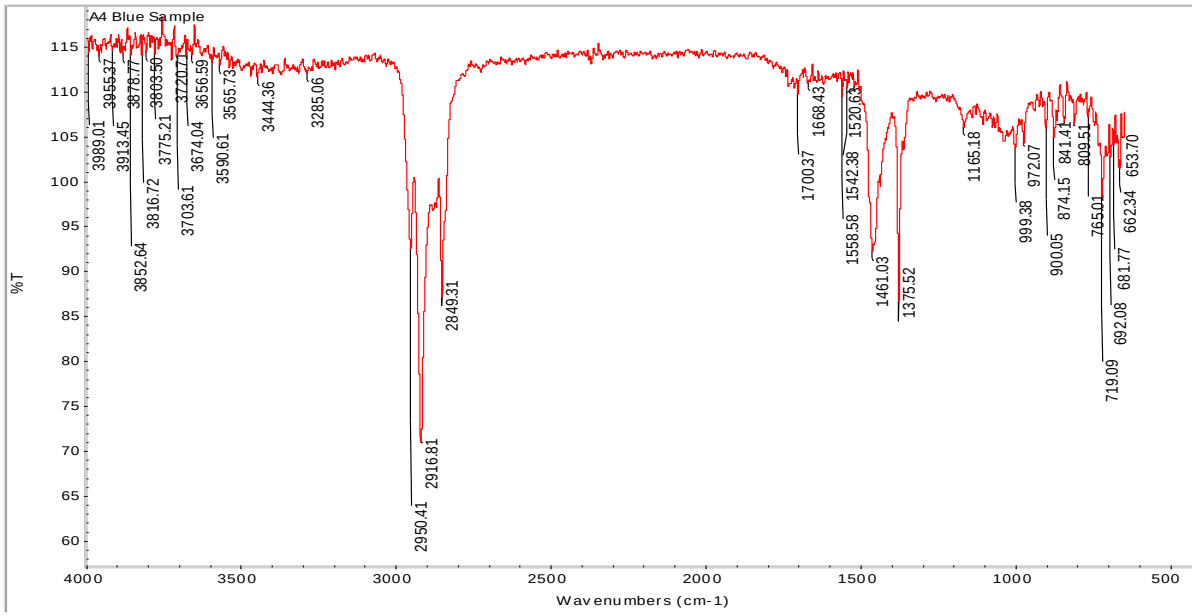


Figure (17): A4 blue sample contains 76.14%Poly (Ethylene), Low Density.

The FTIR spectroscopy (Table1 and Figure 15) shows a 76.14% possibility for the A3 blue sample having the spectra for microplastic compared to the library spectrum. The peaks are between653 and 3,989 cm^{-1}.

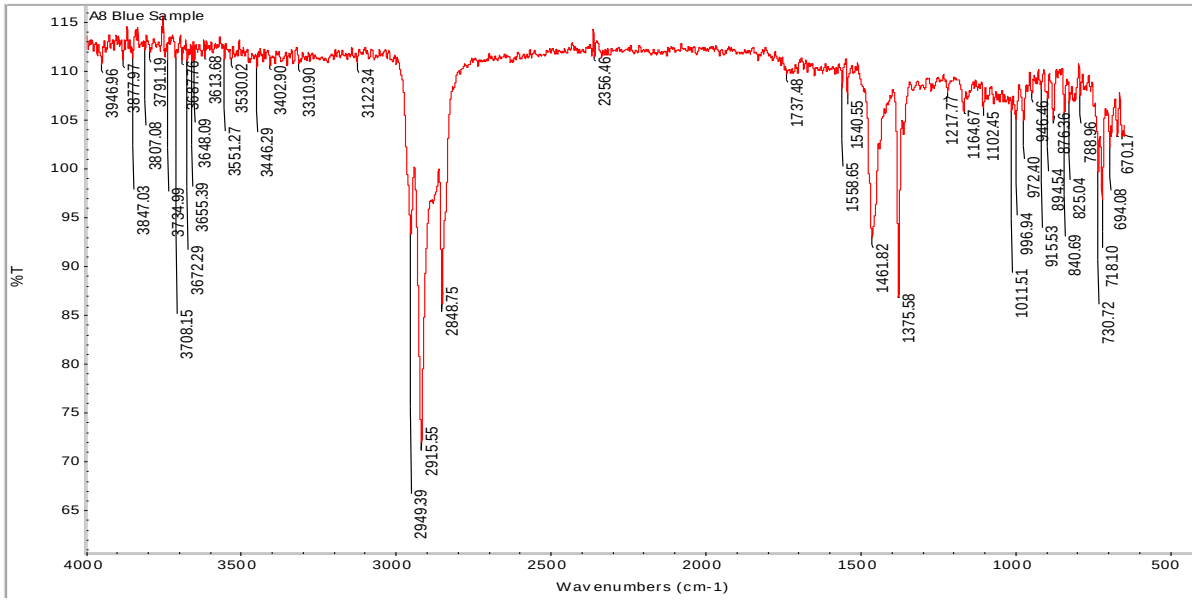


Figure (18): A8 Blue Sample contains 76.1% Poly (Ethylene), Low Density.

The FTIR spectroscopy (Table1 and Figure 18) shows a 76.1% possibility for the A8 blue sample having the spectra for microplastic compared to the library spectrum. The peaks are between 670 and 3,946 cm^{-1}.

Styrene Butadiene Block Polymer (SBBP):

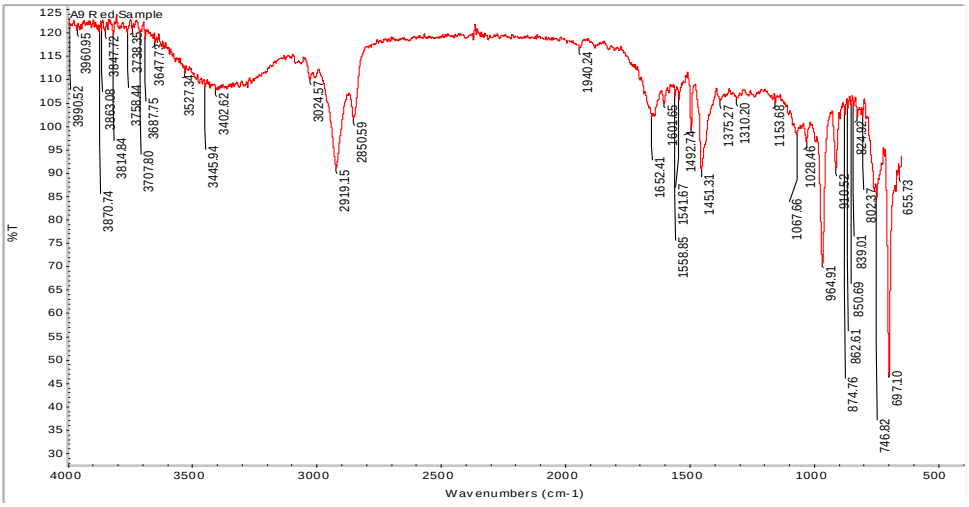


Figure (19): A9 Red Sample contains 72.37% Styrene-Butadiene Block Polymer.

The FTIR spectroscopy (Table1 and Figure 19) shows a 72.37% possibility for the A9 red sample having the spectra for the Styrene-butadiene block Polymer microplastic compared to the Styrene-butadiene block Polymer library spectrum. The peaks are between 655 and 3,990 cm^{-1}.

Discussion:

Microplastics can enter the marine environment directly as primary MPs (such as the pre-production pellets and/or granules used as abrasives in cleaning products) or indirectly as secondary MPs due to the gradual is integration of MPs into smaller fragments in the environment. The relative importance of primary and secondary sources of microplastics to the marine environment is unknown (Ghayebzadeh et al., 2020). One of the key threats of microplastics is possible ingestion by aquatic organisms, which is detrimental to some marine species (Abadi et al., 2019). There is scarce information on the extent of the harmful impacts of microplastics on the ocean environment. Some reported toxic effects of MPs are cell damage, infections, tumor formation, and death (Jafari et al., 2010).

Descriptor 10 of the MSFD for marine litter and its formulation states, “Characteristics and quantities of marine litter do not cause damage to the coastal and marine environment.” This statement is the first European directive addressing marine litter in an integrated manner to protect the marine environment (Galgani et al., 2013a and b). The identification of MP polymer was by comparing the spectra from an unknown sample against that of a known standard polymer in a database. Hummel, D. O. (2002) provides a complete description of this technique. It is worth noting that this method is only definitive when there is a good match, which is not always possible. The biofouling and degradation of microplastics in the environment cause a slight difference in their spectra compared to the spectra of the virgin materials in the library. Therefore, it is pivotal to record the type of polymer when formal particle identification is through Fourier Transformed Infrared (FTIR) or Raman Spectroscopy. Even though spectroscopy is not critical for routine monitoring of fragments larger than 500 µm, it is crucial for fragments > 50 µm. A routine examination of five to 10% of all samples is essential to confirm the relative accuracy of any visual examination. A suitable approach proposed by the TSG-ML is to accept any match with>70% similarity.

Hwang et al., 2020 recommended individually examining the samples with 60 to 70% similarity, rejecting samples without clear evidence of peaks corresponding to the known synthetic materials, and routinely rejecting (as synthetic) any samples with a spectra match of less than 60%. The polyethylene spectra obtained by this study had a match >91.76%,> 74.86% for Polypropylene, >68.49% for Polystyrene, and >72.37% for styrene-butadiene block polymer, as shown by the FTIR results (Table 1). This study recommends confirming the identity of polymers within the size range of1–100µm by subjecting them to further spectroscopic analysis. Confirmation of the identity of suspected MP polymers with sizes ranging from 101 µm–4.99 mm is by subjecting 10% of the material in each size class, up to a maximum of 50 items per year or sampling occasion, whichever is the less frequent, to further spectroscopic analysis, such as FTIR. The confirmation is crucial to ensure quality control of visual identification and gain insight into the relative abundance of different polymer types, which could provide information on their sources. TSG-ML recommends accepting any match with a similarity of over 70%, rejecting samples that do not show clear evidence of peaks corresponding to known synthetic materials, and routinely rejecting (as synthetic) any samples with a spectra match of less than 60%.

Conclusion:

Analysis of the samples from different points at the Port of Tripoli, Libya, showed high pollution levels by PE, PP, P. sty, and other polymers. Based on the analytical data, it is possible to conclude that there was an influx of pollutants from the Mediterranean coast into the sea. Authorities can deal with microplastic pollution, such as PE and PP, by removing them from the environment before they undergo physical and chemical transformation. The low levels of these pollutants suggest that microplastics are present on the beach, and thus, it is imperative to determine their sources. Based on the analytical data, this study predicts that environmental factors, such as soil organisms, sunlight, wind speed, and the chemical composition of the soil and water, affect the transformation of the microplastics in the soil and, therefore, it is essential to conduct a comprehensive investigation of these parameters. The research should encompass larger coastal and sea areas to deepen understanding of the relevant issues.

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