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Occurrence And Identification Of Microplastics In Surface Waters And Sediment Of The Al-Razzaza Lake\ Iraq

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Abstract:

This study was done to investigated the presence of microplastics in water and sediment of Al-Razzaza lake in mid of Iraq. Samples were collected and analyzed seasonally from surface water and sediment during November 2020- July 2021. The analysis of microplastics (MPs) in different environmental samples include detection, imaging and identification of the type of microplastics in the study region by fluorescent technique labeling with Nile Red staining and Raman spectroscopy were used to determine shape and type of MPs. The results clearly show the presence of a large number of MPs in both samples. Fragmants form were dominant in sediment samples it recorded 43%, also fiber or filaments were recorded 22% from all examined MPs, while microfiber and filaments were high percent in water samples 34% and 23.9% respectively, polymer types of MPs according to Raman spectrum identified main type for fibers is polyethylene terephthalate PET in collected samples from studied area. whereas, in fragments shape are acrylonitrile butadiene styrene ABS and poly m-phenylene terephthalamid. The presence of microplastics indicated the Al-Razzaza lake is heavily polluted with plastic pollutants by various sources.so we need to more work to obtain accurate data on microplastics in freshwater of Iraq.

Key words: Microplastic ,Al-Razzaza lake, Raman Spectroscopy, Nile Red.

1. INTRODUCTION

Plastic is now considered one of the basic materials widely used in the daily life of consumer products as well as in industrial processes, due to its being light, durable, low cost, resistant to most chemicals and easy to process, it has been used in many applications since the early twentieth century, the use of plastic has increased in all Over the world, especially in the past few decades, 47 million tons, 288 million tons and 335 million tons were produced in 1976, 2002 and 2015 respectively, and production is expected to double again in the next twenty years and lead to an increase in production Plastic increases the amounts of plastic waste in terrestrial and aquatic ecosystems, and plastic waste can be found all over the world from the Arctic to the Mediterranean and the Pacific (Lagard, et al., 2016)..

It is estimated that 8 million tons of plastic are released into the oceans annually and

most marine plastics come from land-based sources. rivers, streams, and wastewater treatment systems to the our environment, Freshwaters may accumulate a large number of microplastic particles and fibers; yet, freshwater microplastics have received less attention than those in seawaters. Such waters can act as sources (such as waste water discharge, transmitting and carrier media such as river and streams. Microplastics can be found in both lentic or lotic systems, because of considerable differences, they may differ from those found in seawaters can be predictable in quantity (Klein et al., 2018).

Large debris of plastic referred to as "Macroplastic" is a concern for its long-term impact on water bodies, through some mechanisms including entanglement and ingestion, MPs can cause aesthetic problems as well as threatening sailing, fishing and aquaculture. Moreover, they cause injury and death to marine organisms (Cole, 2011), it can induce a variety of negative physical impacts on people and other organisms. Microplastics can carry a variety of poisons, such as additives from industrial manufacturing processes and persistent pollutants, through sorption in water. These poisons have the potential to cause serious health issues in people. Microplastics and their related toxins are bio-accumulated in fish, causing issues such as intestinal injury and changes in metabolic profiles, according to a few studies (Li et al.,2018)

In addition, the increasing quantities of microplastics over the past decade; Microplastics are categorized as small pieces of plastic, generally defined as <5 mm in diameter, resulting from the cracking of larger particles by various factors. The larger pieces are shredded into smaller pieces, resulting in an increase in the surface area of the plastic, and this facilitates the microplastics to move easily within aqueous environments. Other sources of microplastics include microfibers, marine paints, cosmetics, and personal hygiene products made of plastics (Niaounakis, 2017)

Common microplastics include Polyethylene Terephthalate PET, Polyvinyl Chloride, Nylon, Polyethylene, Polypropylene, Polystyrene, and; Representing 95% of global plastic production, these microplastics have negative impacts on ecosystems by entering the food web and acting as a vector for transporting various pollutants that have affinity for plastic surfaces (Lagard et al., 2016) . Microplastic pollution (MPs) in aquatic system has become a global problem currently. However, there is no information available about the plastics pollution of Lake Razaza. So, this is study was done to investigate and monitoring the levels of Microplastic pollution in this lake and determination the types of polymers prevalent in them, as well as established data base for plastic pollution in this aquatic system.

2.Materials and Methods 2-

1 Study Area

AL-Razaza lake were chosen in this research to study the plastic pollution in the Al-Razzaza lake, it is a water body divided between karbala and al-anbar governorates, which received its water from several sources, the most important of which are the northern al-mizel canal for the city of karbala, the extra water of lake al- habbaniyah, the oyoun al-shatatah and al-rahaliyah channels and groundwater in some points.

2-2 Samples Collection:

water samples were collected at latitude and attitude (32.635942, 43.876341) in east lake

near Kerbela city, preparation and analysis of samples from surface water as previously described by (zhang., 2017). briefly, each sample was poured through stainless steel mesh sieves with apertures (0.075 mm). the contents of the sieve were transferred to glass beaker then filter across filter paper (GF 1µ) with vacuum pump, for removing any organic matter and other debris all samples were digested by H_2O_2 (hurley and nizzetto, 2018).

Surface sediment of samples (about 500g) were collected by stainless steel 30 cm container at three replicates, The crushed sediment is mixed with 300 ml of saturated sodium chloride solution in the filter bottles with stirring for 15 minutes, density separation the most widely used method is isolation of microplastics from soil is density separation, filtration the plastic particles are separated from the supernatant obtained from density separation by passing the solution containing the plastic particles through a vacume filter, generally assisted by a vacuum. each filter paper was placed in a clean glass petri dish, covered and stored until further analysis (sulochanan and lavranya, 2014). the particles were examined and analyzed according to the method published by (mu.2019). to break down the natural residues and organic matter H_2O_2 and HNO_3 30% for 24 hours .

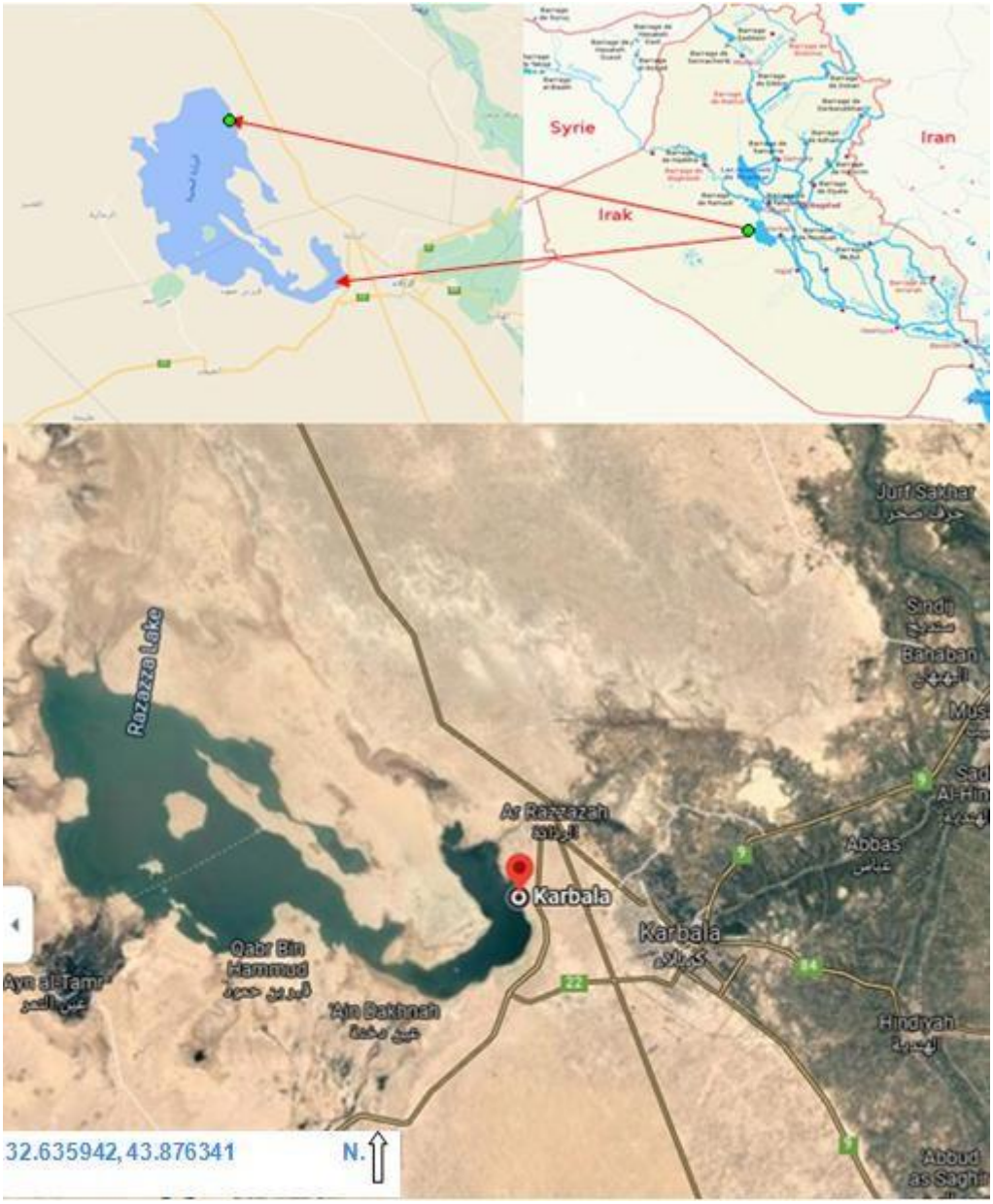


Figure 1: Location and geographical map of the study area.

2-3 Detection and Diagnosis of Microplastics:

2-3-1 : Visual Characterization:

The particles were examined and analyzed according to the method published by (Mu.2019). All particles were subjected to staining with Nile Red for fluorescence microscopy has been used to visual and identified by their color and shape of microplastics (Younk et al., 2016). Nile red was purchased from HIMEDIA company, 5mg of dye was dissolved with 100 ml methanol to prepared staining solution, 2-3 drops of stain were added to the surface of the filter papers and left for 10 minutes, then the microplastic examined by a ZEISS fluorescence microscope (German) under 10x using green fluorescence light with an emission of 522 nm and an excitation emission 488 nm. (Shim et al.,2016; Erni-Cassola et al.,2017)

2-3: Identification of the Type of Polymers:

Raman spectroscopy was used for the chemical and physical characterization of microplastics that are made through this technique to detect and identify of microplastics in the environmental samples. micro-Raman spectroscope (Takram, Iran) with a laser of 785 nm and Raman shift of 220–3900 cm^{-1} has been used to identify the polymer types of MPs. Plastic particles are identified using Raman spectroscopy, by projecting a monochromatic laser beam onto a suspected sample, which leads to different frequencies of the light bounced back due to absorption or intensification. Unique to each polymer and after Raman spectroscopy, a non- destructive sampling technique (Renner et al.,2017).

2-3-Statistical Analysis:

Microsoft Excel software was used to calculate and analyze all data and statistical analysis program (SPSS.Version.16) were used in the Paired T-test at $P < 0.05$ to compare the results obtained for MPs in water and sediment.

3- Results and Discussion

3-1 The Quantitative Study

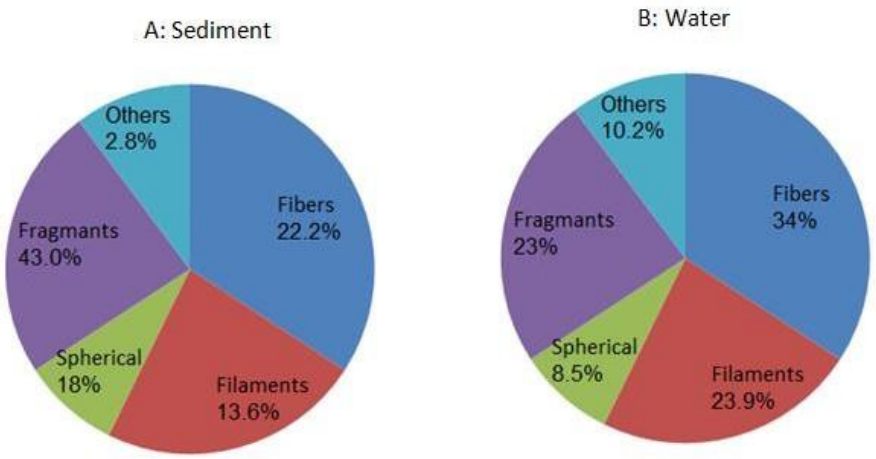
The results of the microscopic examination of the samples showed the presence of microplastics in varying numbers in the study stations of surface water and sediment. the highest value in the water samples of Al-Razzaza Lake in the summer, and the percentage of plastic fibers was the highest among the microplastic shapes, and perhaps the reason is due to the presence of fishing nets abandoned, sewage that is concerned with synthetic fibers, which comes from water washing, and the spherical shape was the most abundant among the known forms of microplastics in the sediment samples, while the highest number of plastic particles was recorded in the sediment samples at the Al-Razzaza lake.

Table 1 :Numbers and shapes of microplastic during the study seasons in the samples of surface waters of Al- Razzaza Lake.

seasons / Shape	Winter	Spring	Summer	Autumn	total
Fibers	85	88	4	3	40
Fragments	82	9	4	2	27
Sphericals	2	2	4	2	10
Filaments	85	4	6	8	28
Others	5	-	2	8	12
Total	49	35	20	13	117

Table 2 : Numbers and shapes of microplastic during the study seasons in the surface sediment of Al- Razzaza Lake.

Seasons / Shape	Winter	Spring	Summer	Autumn	Total
Fibers	22	28	25	22	86
Spherical	27	85	87	88	70
Fragments	44	42	42	44	167
Filaments	87	84	88	82	53
Others	3	2	4	4	11
Total	110	91	96	90	387



Figure(2): Percentage (%) of the observed shapes in the total collected MPs from surface water and sediment in the Al-Razzaza lake.

3-2 The Qualitative study

In this study, fibers, pellets, filaments, and fragments were the main four classes of microplastics. The results showed that fibers 34%) and filaments (23..9%) and were the most abundant form of plastic in water samples, followed by fragments shape(23%) and spherical(8.5%), while the results showed that fragments(43%) and fibers (22.2%)were the highest percentage in sediment samples, then spherical shape and filaments were recorded 1% and 13% respectively. May be the reason for that due to the relation shape of the shape with the buoyancy feature of this particles in the water column. According T-test no significant differences ware detected among all haps in the water and sediment samples (p-value=0.4. at $p < .05$). these results consistent with that found by (Dai et al.,2018). This is probably due to the presence of fishing and tourist activities, local sewage discharge, textile manufacturing, all of which are potential sources of fiber. In addition, more fibers were also found in sediment samples. The difference is that compared to surface water samples, sediment samples contain more fibers. A large amount of fragments and pellets that may result from the small surface - the ratio of the size of the fragments, pellets, allowing them to sink and settle to the bottom. Moreover, these results are consistent with (Eriksen et al.,2013) there are multiple point sources where microbeads may enter the environment which are floating in freshwater systems (some lakes or rivers) with fresh water are close to the areas with high population, where higher microplastics abundance was detected.

3-3 Fluorescence technology in detection and diagnosis of MPs

The results of current study showed that microplastics fluorescent on the filter papers with sizes ranging from (1-65µ) according to mesh of sieves and Millipore of filter papers. Our preliminary results indicated that the abundance of microplastics in

sediments may have been underestimated previously. Fragmants form were dominant in sediment samples it recorded 43% , also fiber or filaments were recorded 22% from all examined MPs, While microfiber and filaments were high percent in water samples 34% 23.9 respectively, Since the amounts of microplastics in the sediment samples were many enough under the fluorescence microscope, the fluorescence technique can be used here as a standard method for counting microplastics or in combination with Raman devices for detection and determination of polymer type, the very small amounts of Nile Red dye adsorbed on the particles do not interfere with Raman spectroscopy, It is easy and inexpensive to apply universally in laboratories with basic equipment for the quantification of plastics. Extremely small objects up to a few micrometers are detected on high-quality images, and thus the sizes are determined by magnification and optical resolution. Already at this stage, sufficient microplastics for optical counting have been detected and these results are in agreement with that of Maes et al. (2016), although the present method as described provides a simple and effective dyeing method for visualizing microplastics. With appropriate modifications to the protocol, from filtration steps to reducing water sample volumes or digestion methods to disposal of organic residues with solvents generally applicable to living organisms, the method should also be applicable to other samples in which microplastic analysis is desirable, reducing cost and speeding up quantitative measurements.

3-4 Identification of the Type of Polymers:

Several studies were used Raman micro-spectroscopy to identify polymer types of MPs in the different environmental samples by vibrational fi p , which is unique for every polymer type, (Manbohi et al., 2021; Kavya et al., 2020 ; Araujo et al.,2018). polystyrene (PS), polyvinyl terephthalate (PPT), polypropylene were detected in the studied samples. Typical Raman spectra of some selected samples are shown in the figure (4), In general, the polymer types indicated a lower diversity compared to those reported in the other regions of the world. These types of polymers are among the most abundant polymers in environmental samples (Anger et al., 2018), PET, or polyethylene terephthalate, is a crude-oil derived synthetic polymer that is today one of the most widely used plastics (Liu et al., 2019). PET output was more than 30 million tons in 2017. (PlasticsInsight, 2017). In 2016, around 485 billion PET bottles were produced, with an expected 583.3 billion plastic bottles being produced in 2021. (Garside, 2019). This polymer is made up of terephthalic acid (TPA) and ethylene glycol repeating units (EG). Besides the types of thermoplastic resin (Di and Wang, 2018) which are widely used in hundreds of industries such as household and cosmetic packaging (Wang et al., 2017). These polymers can be easily introduced into the environment through the discharge of domestic and industrial waste and corrosion (Andrady and Neal, 2009). Fishing activities, tourism and sewage from neighboring residential areas are the main sources of polystyrene in the studied samples**.** as all industrial polymers from any fragments exposed to UV radiation, weathering, abrasion, as well as chemical and (micro)biological degradation

may be that caused breakdown of macroplastic to release micro and nano plastic continuously, this makes these MPs for ingestion by aquatic animals as floated particles which may experience a variety of physiological changes with long term or short exposure by type of polymer (Bhattacharya and Khare, 2020).

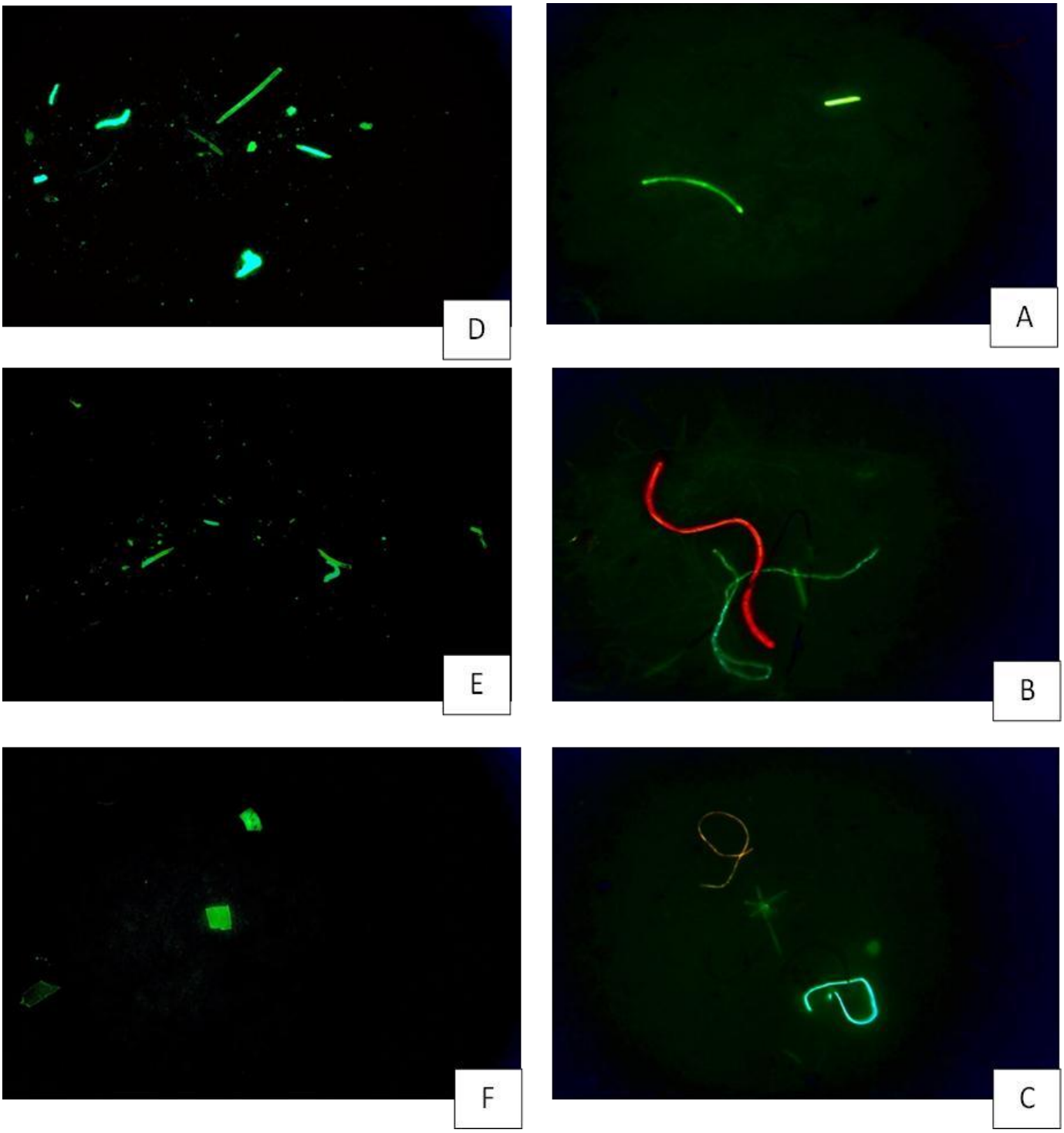
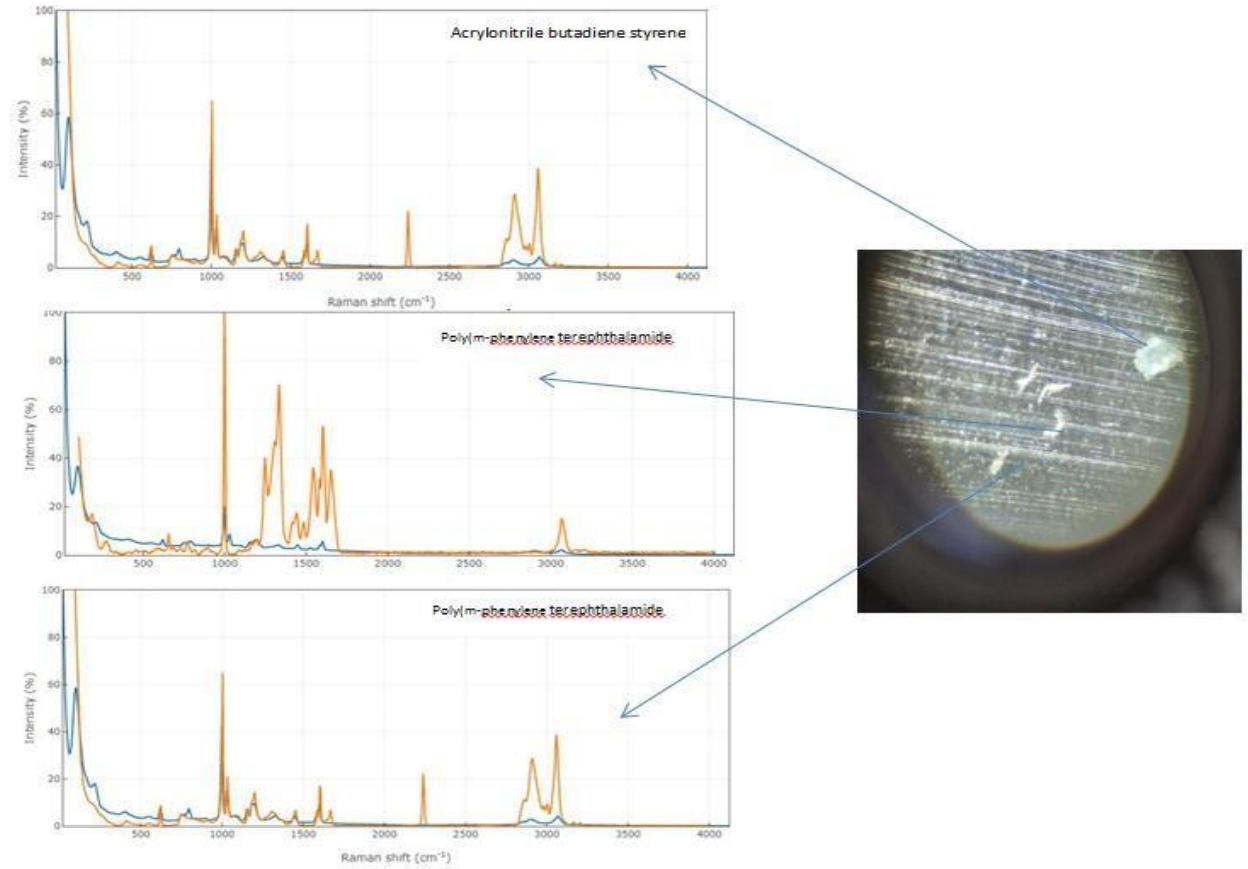
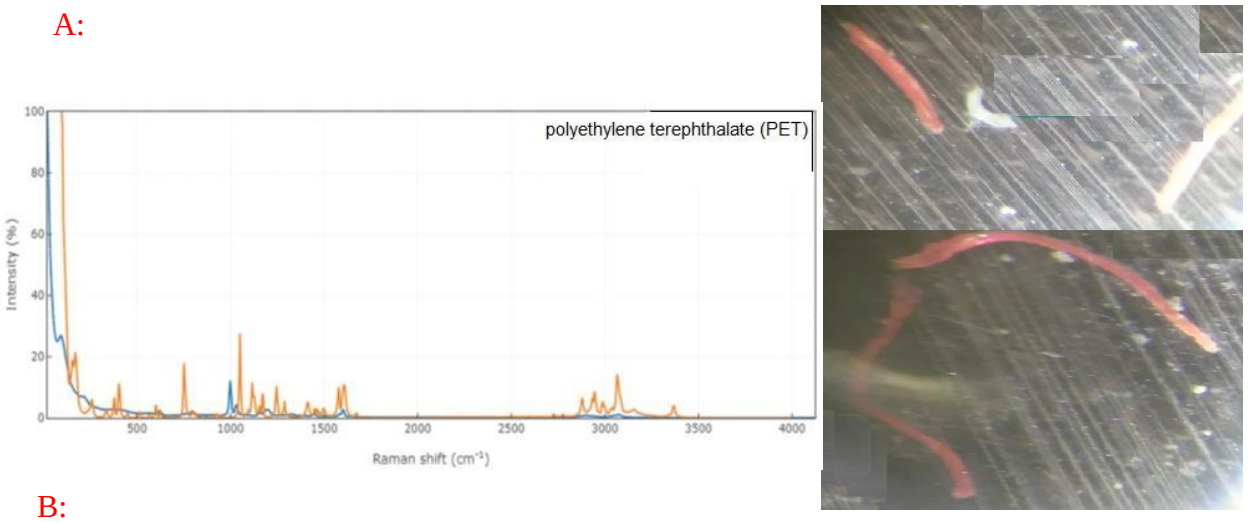


Figure3: (A,B,C) images of MPs under fluorescent microscope in water (D,E,F) in sediment



A:



B:

Figure 4:Selected Raman spectrum for identified type polymer of MPs in Sediment Fragments (A:acrylonitrile butadiene styrene (ABS); poly(m-phenylene terephthalamide) in Water(B: polyethylene terephthalate PET (fibers)for collected samples from studied area.

4- Conclusions and Recommendations:

MPs pollutants in freshwater that are becoming increasingly problematic required monitoring, assessment and determination of fate, sources and environmental risk associated with MP. Larger plastic products breakdown into so-called microplastics (MP), which are pieces with a diameter of less than 5 mm when exposed to the environment. Because their bioaccumulation potential with decrease their size, MP is ingested by plankton, fish, birds, and even mammals, and accumulates in the aquatic food chain (Wright et al.,2013)**.** Accordingly, the results of the current study came as the first study to prove the pollution of Al-Razzaza lake with microplastic pollutants, as it receives its water from different sources, including sewage and treated and untreated wastewater, as well as surface torrents in the rainy season to wash away soil surface pollutants, especially near populated cities as well as from sites that pass solid waste. polyethylene terephthalate PET are dominant polymer species in study area which are widely used in hundreds of industries as packaging material. One of the important observations that have been recorded is that Al-Razzaza lake is heavily polluted with plastic pollutants and from various sources. Thus, it is necessary to expand further studies on the fate of these pollutants and investigated to the nanoplastics in this water system.

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