Microplastics (MPs) distribution in Surface Sediments of the Freidounkenar Paddy Wetland

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Abstract

There is an urgent need to increase knowledge on the distribution of microplastics (MPs) in wetlands because these are sites of special ecological value and the ever-growing use of plastic can threaten such fragile ecosystems. This research assesses, for the first time, the occurrence of MPs in surface sediment of the Freidounkenar International Wetland (Nothern Iran), a valuable habitat for migratory birds. A total of 1368 MPs/kg were identified in the surface sediments of the wetland. The distribution of MPs in sediments per area was Ezbaran (36.5%), Western Sorkhrood (32.0%), Freidounkenar (20.1%) and Eastern Sorkhrood Ab-bandans (11.4%). The most contaminated sites were located close to agricultural fields, Damgahs (agroecosystems for birds), fishing areas and roads. Fibers and white-transparent and black-gray MPs constituted the dominant MPs in the surface sediment. The most abundant MPs were < 250 µm and these were made of nylon, polypropylene - low density polyethylene copolymer, polystyrene, low density polyethylene and polypropylene. The identification of MPs was carried out visually and supported with Scanning Electron Microscopy (SEM)-Energy Dispersive X-Ray (EDX) and micro-Raman techniques. There were weathering signs in large proportion of the MPs, according to SEM analysis, which evidences their formation from the degradation of other plastics. This is a comprehensive study on MPs in surface sediment of this sensitive internationally recognized ecosystem with high ecological value.

Keywords:

Mazandaran; Agriculture; Sediment; Plastic pollution; Fiber

Highlights

- This study is the first comprehensive research on MPs in the Freidounkenar Wetland.
- MPs were detected in all sampling sites (23 – 86 MPs/kg).
- The highest MP concentrations were detected in Ezbaran Ab-bandan.
- Fibers (< 250 μm) were dominant.
- Agriculture activities may lead to an increase of MPs entering wetland.

1. Introduction

Wetlands are important environments that occupy transitional zones between terrestrial and aquatic ecosystems. They provide critical ecosystem services and value for human well-being. Some important services that wetlands provide include water, water purification, food supply, flood control, pollution control as well as having aesthetic and recreational value (De Groot et al., 2006). Wetlands act like extensive sponges for pollutants as well as excess water. However, anthropogenic disturbance, deficient waste management systems and lack of understanding in managing and maintaining wetlands have led to considerable loss, conversion and deterioration of these useful ecosystems (Groot et al., 2018).

Plastic products are firmly integrated in the daily life of our societies due to their properties including flexibility, persistency, waterproof, lightweight and low cost (Wong et al., 2020). Plastic exposure to various environmental factors such as heat, ultraviolet light or microbial communities cause polymer degradation in nature (Ray et al., 2022). Among different types of plastic debris there are microplastics (MPs): solid polymer particles < 5 mm which are emerging as a serious environmental threat and have already attracted the attention and concern of many sectors including public media, scientists and governmental institutions (Law, 2017). The reason for the alarm on MP pollution is its persistence, potential toxicity and the global increase in the production of plastic products that can lead to even greater MP pollution (Rochman et al., 2016). Polypropylene (PP), polyethylene (PE), polystyrene (PS), polyvinyl chloride (PVC), nylon (NY) and polyethylene terephthalate (PET) are widely used due to their versatile applications (An et al., 2020). Secondary MPs result from the breakdown of bigger plastic items. In contrast, plastics prepared originally in MP size, such as microbeads in cleaning and cosmetic products or plastic resin for commercial use, are classed as primary MPs (Du et al., 2021). Microplastics occur in different forms, colours and compositions.

In the absence of efficient management and removal mechanisms of plastics waste, MPs have rapidly become ubiquitous due to their widespread industrial, medicinal, municipal and commercial applications (Wright et al., 2013). As a result, MPs are detected in many ecosystems around the world (Daily and Hoffman, 2020). Wetland ecosystems are considered a particular hub for MPs accumulation as they are vulnerable to debris deposition from terrestrial and marine systems (Birami et al., 2020). Therefore, MPs may pose a risk to communities, populations and ecosystem functioning. While several types of MPs with densities lower than seawater (1.02 g/cm^3) tend to float in the water column or on the sea surface, MPs with higher density can easily sink and accumulate in sediments (Uddin et al., 2021). Processes like biofouling can also increase the density of light MPs and favor their presence in sediments (Soltani et al., 2022).

The Freidounkenar wetland is located in the southeast of the Caspian Sea, in the Mazandaran province. The wetland plays an important socio-economic and ecological role in the region: water supply for aquaculture and irrigation; tourism; habitat of diverse species; and it mitigates the migration of birds to urban sites. This wetland includes harvested rice paddies that are shallow freshwater habitat. These host the western Siberian crane, along with several species of waterfowl, especially dabbling ducks and geese in winter, and many fish species (Ahmadpour et al., 2011). Hence, finding information on the MPs affecting that ecosystem is a milestone in the environmental management of this international wetland. The aim of this study is to investigate the occurrence and distribution of MPs in the surface sediments of the Freidounkenar Wetland and relate that pollution with its broad origin. This study will help to understand more MP pollution and the assessment of its ecological risks in wetlands. It will inform decision-makers seeking to restore wetlands.

2. Materials and Methods

2.1. Study area: The Freidounkenar Wetland

This research was conducted in the Mazandaran province and on the southern Caspian coasts in central regions of the Alborz highlands in the north of Iran (Fig. 1). This region has a humid temperate climate, with annual average temperature ~25° C in summer and 6° C in winter, and an annual average rainfall of 749.9 mm (Ministry of Energy Iran, 2015). Agriculture, tourism, fishery and textile industries are the main economic activities in this province.

The Freidounkenar Wetland covers 5427 hectares, and it is the 22nd International wetland of Iran and the 2nd largest wetland in the Mazandaran province. It is registered in the Ramsar convention (Ahmadpour et al., 2011). This wetland includes significant regions which are known as Damgah (trap place) in Iran. Damgahs are recognized as low slope plains devoted to rice cultivation where migratory birds live during cold seasons. In many instances, they are restricted by barriers made by straw to keep birds calm away from traffic. Freidounkenar Wetland comprises four "Damgahs" or birds catching units including Freidounkenar, Ezbaran, Eastern and Western Sorkhrood Ab-bandans. These Damgahs are like small islands located inside a large ecosystem which includes a complex of shallow freshwater preserved in harvested rice paddies and provides an excellent feeding habitat for large number of birds (Ahmadpour et al., 2012) (described in Supporting information S1). The areas comprised with Freidounkenar, Ezbaran and Sorkhrood Ab-bandans is surrounded by 350 hectares (Ahmadpour et al., 2011). Rice crops are the main crop in the wetland and they are managed by farmer cooperatives (Mirzaei et al., 2019). This wetland is surrounded by agriculture, aquaculture, road construction and rural areas. A large volume of wastewater discharge from the rural area enters the wetland.

2.2. Sample collection and MPs extraction

Sampling of sediment in Freidounkenar Wetland was carried out between the 5th and the 17 th of September (2021). Sampling sites were selected considering predictable hotspots of MPs pollution based on agricultural farms, rural areas and across the surface area of four Ab-bandan (described in Supporting information S1).

Sediment samples were taken from the upper ~5 cm of the bed sediments from 28 sites using a stainless Van Veen grab sampler and a stainless-steel shovel. Considering the surface area of each Ab-bandan 10, 5, 10 and 3 sediment samples were taken from Ezbaran, Freidounkenar, Western Sorkhrood and Eastern Sorkhrood, respectively (Fig. 1). At each sampling site, ~1 kg of composite sediment sample (comprising a mixture of four subsamples taken within a radius of 1 m) was collected, homogenised and finally wrapped in pre-cleaned aluminum foil and sealed in a zip-lock bag until further treatment. The collected samples were then transferred to the laboratory and stored at room temperature for analysis. Nitrile gloves and cotton coat were used throughout the sampling.In the laboratory, sediment samples were spread on aluminum foil sheets and let to be air-dried at room temperature until constant weight was achieved. Digestion of the sediment samples with hydrogen peroxide was carried out to eliminate organic matter attached on MPs (Zobkov and Esiukova, 2017). For this purpose, 200 g of each sediment sample was sieved (5 mm cut-off) and mixed with 200 mL of 35% H_2O_2 solution in a glass beaker and let to stand for 15 days to degrade organic matter. When the reaction was complete, each digested sample in a glass beaker was covered with an aluminum foil and let dry on a sand bath at 60 °C for 8 h. Using the density separation method, MPs were made to float by adding 70 mL of $ZnCl_2$ solution (1.6 – 1.8 g/cm^3) (Konechnaya et al., 2020). After shaking the beakers for 15 min, they were allowed to settle overnight to let the sediment particles settle while MPs stay in suspension or floated. The separation of MPs was carried out by centrifuging the supernatant (5000 rpm for 5 min) . The remaining solution was filtered through S&S cellulose filter paper grade 589/3, blue ribbon, pore size < 2 μm using a vacuum pump. This procedure ($ZnCl_2$ solution, centrifugation, and filtering) was repeated three times for each sample. All filter papers were covered with aluminum foil throughout the filtration process to minimize contamination. Finally, the filter papers were left to dry in pre-cleaned, uncontaminated chiffonier in a sterilized and secluded room with controlled air circulation. Dry MPs on each filter were placed into a glass petri dish with lid until analysis. Throughout all these preparatory steps, precautions were taken to avoid background plastic contamination.

2.3. MPs identification

Visual inspection served as the first step in identification and quantification of MPs. It was carried out using a binocular optical microscope with up to 200 x magnification (Carl-Zeiss, Oberkochen/West Germany) which aided the counting of MPs along with identifying diagnostic features such as size, shape and colour (Hidalgo-Ruz et al., 2012). Microplastics were classed as fibers, fragments, beads and foam. Size categorization (L) was based on the longest dimension of each particle (100 μm < L, 100 ≤ L < 250 μm, 250 ≤ L < 500 μm, 500 μm ≤ L < 1000 μm and ≥ 1000 μm), and the classification of MPs by colour comprised five groups (yellow-orange, white-transparent, black-grey, red-pink and blue-green).

Identification of MPs was also done using an SEM-EDX (TESCAN Vega 3, Czech Republic) mostly to reveal the surface morphology and determining the elemental structure of polymers along with additional information on their inorganic additives (Girão, 2020). MPs' polymer type was determined using a micro-Raman microscope (Lab Ram HR Evolution, Horiba Japan) equipped with a 785 nm laser and detection between 400 – 1800 cm^{-1}. For this purpose, MPs were mounted on to double-sided copper adhesive tapes and coated with gold for SEM-EDX analysis. A 8% of the total MPs were further characterized with SEM-EDX and micro-Raman microscopy.

2.4. Prevention of contamination

To minimize the risks of contamination during sampling, sample processing and analysis, precautions were implemented to ensure that the generated data were accurate and reliable (Brander et al., 2020). Throughout analyses, the use of plastic containers and tools (e.g. laboratory equipment) was avoided and replaced by stainless steel shovels and glass bottles. Furthermore, to ensure a working environment was free or with reduced plastic contamination, all tools and materials were rinsed three times with pre-filtered water and one time with 96% ethanol. Materials were cleaned once more before touching the next sample to decrease contamination risks (Prata et al., 2021). Before use, glass utensils were washed with phosphate-free soap; double rinsed with distilled water and left in nitric acid (10%) for 24 h. Finally, they were rinsed three times with double-distilled filtered water and left in pre-cleaned cabinets to dry at room temperature. Cotton lab coats and powder free nitrile gloves were used during the whole laboratory process in order to control fiber contamination (Wang and Wang, 2018). To avoid MP contamination from air, a series of protocols were implemented including working under clean room conditions with controlled air circulation as much as possible. Clean filter paper, materials and samples were covered with aluminum foil.

Quality control was checked by having four separate filter papers in glass petri dishes on the lab working bench (as a control blank). The absence of plastic particles in the blanks taken and processed during sample treatment and MP charactersation steps indicated that risk of sample contamination was negligible.

2.5. Statistical analyses

Arc GIS 10.3 software was used to map spatial distribution of sampling sites. All statistical analyses were conducted the Microsoft Excel 2016 and SPSS 26.0 software (IBMCo. Ltd., USA). The graphs were created using Excel 2016 software. Normality distribution of MPs abundance was checked using Kolmogorov–Smirnov and Shaphiro-Wilks tests.

3. Results and discussion

3.1. MPs distribution and sediment contamination

A total of 1368 MPs were detected in 28 sediment samples. The number of identified particles in sediment was 23 - 86 MPs/kg, with mean and median being 49 ± 15.43 and 46 MPs/kg, respectively. The detailed characteristics of the MPs found in the sediment samples are given in Supplementary material Table S1. Statistical analysis was carried out to assess the normality of the number of MPs quantified in sediments. A normal distribution was found ($p > 0.05$) with

Kolmogorov–Smirnov (0.113 > 0.05) and Shaphiro-Wilks (0.244 > 0.05) tests. There have not been standard procedures for sampling sediments until today. According to studies conducted by Wang et al. (2019) the top layer sediment (1 - 5 cm) present the highest concentration of MPs than the top 10 cm, and MPs abundance decreased with increase sediment depth. In this way surface sediments (1 - 5 cm) were used because they could better describe MP pollution.

The highest concentration of MPs in sediments (86 MPs/kg) was counted from site F8, location that corresponded to Ezbaran Ab-bandan, close to Ezbaran village. It is the nearest inhabited area, closer to the road, among all the sampling sites. In contrast, the lowest level of MPs (23 MPs/kg) was found in F20 (Western Sorkhrood Ab-bandan), which is smaller than the other Ab-bandans studied: it also has smaller population than the other study sites and has low traffic. Plastics can be washed from land by direct inputs from precipitation, wind or main sources of contamination (Duis and Coors, 2016). As reported by Vogelsang et al. (2018), surface wear of car tyres, road marking paints and road pavement containing polymer-modified bitumen were identified in previous studies as abundant sources of MPs and and were expected to be transported to wetland systems through road runoff and stormwater. The abundance of MPs in Ezbaran, Western Sorkhrood, Freidounkenar and Eastern Sorkhrood Ab-bandan follows the decreasing order of 36.48%, 32.02%, 20.10% and 11.40% in sediment samples, respectively. The high abundance of MPs in the Ezbaran Ab-bandan site could be due to its proximity to an inhabited area, roads and tourism activities. The link between population density and MP pollution was also proposed from wetland sediments in Melbourne, Australia (Townsend et al., 2019). In the study area, the use of plastic mulches and potentially MP-contaminated compost in agriculture and horticulture activities can result in MP release to the wetland (Scopetani et al., 2022; Gui et al., 2021). In addition, based on the semi-closed morphology of the Ab-bandans, the MPs released may remain in wetland for a long time. Hence, the MPs, together with potentially adsorbed heavy metals and hydrophobic organic pollutants, can be transferred and accumulated in biota. In addition, insufficient infrastructure for treating wastewater generated by households, agriculture and rainwater outflows, as well as poor waste management regulations, are widely recognized as significant contributors to MP pollution. Annually, millions of rare migratory birds spend the winter in the Freidounkenar Wetland, with estimated 3000 birds killed daily by illegal local hunters to be sold at local markets. Thus, plastic particles from the degradation of plastic bullet cases or bird catching nets could also form and spread in the environment. A comparison of the frequency and properties of MPs in sediment of the Freidounkenar Wetland with other wetlands and aquatic systems in the world are presented in Supplementary material Table S2.

The abundance of MPs in this study is much lower than that in western Norway (Haave et al., 2019), which constitute an extreme of pollution. Furthermore, the Freidounkenar Wetland recorded lower sediment MP abundance and distribution compared to mangrove wetlands of China, Poyang Lake of China and the Anzali Wetland in Iran (see Supplementary material Table S2). NY, PE, PS, PP were the main polymers found in sediment of the study wetland, and also in most reviewed studies, and fibers were the dominant shape of MPs across studies. In our researched area, PE, PP and NY fibers were probably derived from clothing , bird catching nets or fishing gears.

3.2. MPs characteristics

Shape, size, colour and the surface chemistry of the MPs extracted from the sediment samples were determined as major characteristics that are related to the source of pollution and also can provide information about the ageing suffered. As an example, representative MPs identified with optical microscopy are displayed in Fig. 2.

The abundance of various MP shapes found in sediments of four Ab-bandans (corresponding to a surface of 350 hectares) of Freidounkenar Wetland are shown in Fig. 3. In all these sites, four shapes were recognized: fibers (48.0%), spherules (40.7%), fragments (10.9%) and foams (0.4%). Similar trends were also detected in sediments of other Ab-bandans (Fig. 3). The results clearly show that fibers are prevalent in the wetland environment and are consistent with the formerly reported data from Hashilan Wetland in Iran (Abbasi, 2021).

The release of MP fibers from domestic effluents, from laundry, is suggested to be an important factor releate to the MPs in this study. Frias et al. (2016) reported that ≈ 2000 MP fibers could be released by washing a single item of cloth made of synthetic fibers. The low density of such fibers is probably a major factor in their ubiquity in the natural environment and making up to 90% of global MP concentrations in the marine environment (Woods et al., 2018). Furthermore, the degradation of birds or fish catching gears, like nets and ropes, as well as atmospheric deposition and materials used in agriculture should also be considered as other input routes of MP fiber pollution (Rodrigues et al., 2018). The presence of spherules (also called microbeads) here was surprising since, unlike fibers, they had not been found to be a major type of MP in other recent studies in freshwater (Soltani et al., 2022); in urban or industrial soils (Nematollahi et al., 2022) or in coastal sediments (Jahromi et al., 2021) in Iran. Microplastics spherules and beads are already shown to originate from personal care products elsewhere and correlated with volume and flow rate of wastewater (Hidayaturrahman and Lee, 2019). Townsend et al. (2019) indicated that the occurrence of microbeads confirmed the entrance of sewage in the wetlands. As shown in Fig. 3, spherule MPs were detected in all Ab-bandans. Foam MPs associated with packaging were also observed in some sediments elsewhere (Lozano et al., 2021) (see Supplementary material Table S1). Moreover, the application of fertilizers along with the use of pesticides (Ahmadpour et al., 2016), and plastics to protect or tie the plants, may leave plastic materials in the crops. These plastics degrade with time and atmospheric conditions, and end up releasing fragment MPs to the Freidounkenar Wetland. The use of sewage sludge to supply nutrients could also be a route of entry of MPs to the environment, that eventually will migrate to the wetland. For instance, elsewhere, it was noted that 3,000 to 430,000 tonnes of MPs annually accumulate in European farmlands through sewage sludge (Nizzetto et al., 2016).

In this research, MPs 100 µm - 250 µm accounted for 94.73% among all the detected MPs (Fig. 4). The dominance of fibers, fragments, spherules and foams with the length of 100 µm -250 µm was 83.99%, 95.65%, 97.61% and 100%, respectively. These results are in agreement with what was reported in Hashilan Wetland, Iran (Abbasi, 2021). The concern about these small fractions of MPs continues to grow mostly due to voluminous plastic waste discharge in wetlands where contact with aquatic species and birds takes place. The small size increases the probability of being mistakenly ingested by aquatic organisms, and thus induce negative impacts especially on fish and birds (Smith et al., 2018). Furthermore, small size MPs can have a great adsorption capacity for trace elements and persistent organic pollutants due to large specific surface area (Bradney et al., 2019). Finally, the smaller the MPs the easier they can be transported by wind and water (He et al., 2019). MPs ultimately could impact human health through consumption of contaminated seafood. Hence, the presence and ecotoxicological impacts of MPs in fish may threaten human health (Barboza et al., 2018).

The MPs in the wetland had a wide array of colours, the most common ones are quantified in Fig. 5. The less colorful ones where the ones more abundant: white/transparent (34.7%) and black/grey

(31.1%)). The MPs with the most vivid colors were less common (yellow/orange (22.1%), blue/green (7.7%) and red/pink (4.4%), where the colour percentages giver have been averaged across Ab-bandans. With the exception of the Western Sorkhrood Ab-bandan, the sediments from the rest of Ab-bandans show a similar trend of MPs abundance based on colour classes (Fig. 5). The colour of MPs can be indicative of their origin (Zhang et al., 2020). Fishing and plastic products like plastic bags and food boxes may be the reason for the high abundance of white-transparent MPs. Transparent fibers have been a very common type of MPs in this study. These fibers could have originated from fishing or bird catching lines and nets. Coloured MPs could be derived from plastic items such as clothing, packing material. Materials used in agricultural products an practices may have contributed to black MPs, as indicated elsewhere (Campanale et al., 2019). For instance, rice seedlings baskets largely used to keep rice seedlings before transplantation in the paddy field are black. Ballent et al. (2016) proposed that black MPs fragments were tyre wear particles. Also, black and blue colours are the standard colours in fishery-related tools and activities (Choong et al., 2021). Furthermore, weathering processes may change the surface colour of MPs (Liu et al., 2020). It was noted that aquatic species often ingest transparent MPs (Bagheri, et al., 2020). However, other researchers propose that the colour of MPs may be the reason for being mistakenly eaten as food by aquatic organisms which may inflict harmful effects on biota (Koongolla et al., 2020).

3.3. Morphology and elemental composition of MPs

SEM-EDX micrographs from different MP are presented in Fig. 6. In the natural environment, MPs are exposed to different weathering processes, which may change their surface and enhance the release of additives (Gewert et al., 2018). In addition, the chemical and physical properties of the surface of plastic particulates play a significant role in the adsorption of trace elements (Rochman et al., 2014). There appears to be a positive relationship between increasing surface area with (when decreasing in particle size), presence of anionic active sites at the surface, porosity, and the ability of MPs to sorb trace elements (Bradney et al., 2019). Weathering results in the generation of cracks and increasing the fragmentation (Veerasingam et al., 2016). Also, physicochemical properties of MPs can significantly change with time. Regarding the shape classes of MPs, it may be said that particles with sharp edges and less smooth surface likely indicate recent break-up from larger pieces or recent introduction into the ecosystem. In contrast, smooth and uniform surface indicate prolonged exposure time. Thus, weathering contributes to MPs acting as contaminants carriers and thus impose deleterious effects on organisms (Hidalgo-Ruz et al., 2012). In the investigated samples, MPs displayed complex surface morphology including smooth, avulsions, rough, cracks, wrinkles and irregular surfaces. Hence, most MPs seem to have experienced different levels of mechanical erosion, chemical weathering and reveal weathering signs that indicate that some are indeed secondary MPs. These results are consistent with assumptions given from sediments from a mangrove wetland in China (Deng et al., 2020). It must also be noted that due to the Ab-bandan semi-closed environments, the investigated MPs in this study have been residing in the wetland for a long time. Apart from high percentages of carbon and oxygen as the main constituents of MPs, trace amounts of other elements including Si, Al, Ca, Cl, K, Mg, S, N, Zn, Fe, Cu and Pd were also detected in some analyzed particles as shown in Fig. 6. The Zn detected could be from the flotation step during sample treatment.

Laboratory research concluded that metals can have a higher affinity for weathered plastic (secondary MPs) than virgin MPs (Turner and Holmes, 2015). Wang et al. (2017) noted that, during polymer processing, additives are a source of trace elements on the surface of processed particulate plastics. For instance, silica is commonly used to improve MP's resistance to abrasion, while Pb, Zn, Co, Cr, Ti and Cd are used as inorganic pigment-based colorants (Bolgar et al., 2007). Most plastics additives are physically added into polymer components and do not react with polymer matrix, hence, are easily released into the environment when discarded (Hu, et al., 2021). On the other hand, Abbasi et al. (2019) reported that some chemicals used in sample treatment, such as $ZnCl_2$ or NaI could have some effect on the elemental composition of the analyzed MPs. Moreover, presence of clay minerals in the sediment may also lead to the occurrence of Si, Al, Ca, Mg, Na and Cl in EDX results. It is thus becoming increasingly clear that MPs provide a major matrix for transporting metals in the ecosystem. Indeed, the abnormally high levels of Cd, Cr, Mn, and Pb detected in feathers from migratory birds in the study wetlands in the past (Karimi et al., 2016) could have their origin, in part, in the degradation of MPs, although this remains speculative.

Mostly the organic functional groups at the surface of the MPs are related to their micro-Raman spectra (Fig. 7). Regarding the polymer composition, NY (36.84%; fibers and spherulitic MPs), PP-LDPE copolymers (26.32%; blue, black, red fibers along with blue fragments MPs), PS (15.79%; black and blue fibers and yellow spherules MPs), LDPE (10.53%; white fibers) and PP (10.53%; white fibers and blue fragments of MPs) constitute the most abundant MPs in sediment. Light weight MPs comprising PP (density 0.85 – 0.93 g/cm^3) and PE (density 0.91 – 0.93 g/cm^3) tend to be suspended in water columns in comparison to higher density MP (Tang et al., 2022). Polystyrene and NY with the density 1.05 – 1.15 g/cm^3, along with light weight MPs such as PP and PE were extracted from sediment samples. Driedger et al. (2015) noted that dense MPs are prone to settle after entering the marine environment. The accumulation of low-density MPs in sediment may be because of changes in the density of MPs through process like biofouling, weathering, biomolecule adsorption and hetero-aggregation (Lobelle and Cunliffe, 2011). Also, additives and foreign materials are another factors that will increase the density of MPs.

Nylon is mostly used in fishing nets and fishing threads due to its high strength and abrasion resistance (Tang et al., 2021). So, various fishing or water bird catching traps in the Freidounkenar Wetland could be the reason for the occurrence of a large amounts of poly MPs, while the area not receiving treated or untreated greywater or having densely populated areas nearby.

However, PP and PE are the most abundant plastics used in urban, agriculture, food packaging, and fishing tools, mostly due to easy processing and low cost (Phuong et al., 2018). PE abundance in the environment is mostly due to its durability due to weaker photodegradability (Zhu et al., 2020). Low-density polyethylene (LDPE) is mostly used for the production of reusable bags, trays, containers, agricultural and food packaging (PlasticsEurope, 2015). Thus, the use of rice seedlings baskets in the Freidounkenar Wetland, could be the reason for high LDPE content. PS is generally used in packaging and manufacturing industries including cosmetics, drinking cups and electronic products mostly due to its insulating properties (Sastri, 2010).

4. Conclusion

MP contamination in surface sediment of the Freidounkenar Wetland can originate from various unsustainable activities in the limit of wetlands based on agricultural farms, indiscriminate use of chemical pesticides and fertilizers, fishing, indiscriminate hunting of animal particularly migratory birds and rural areas. However, due to the complexity of the transport and conversion of MPs in the natural and urban environment, it is relatively difficult to define the exact source of MPs. The greatest abundance of MPs found at a site (Ezbaran Ab-bandan) can be due to its proximity to Ezbaran village and tourism activities. White/transparent microfibers made of NY, LDPE and PS were dominant types of MPs in the Freidounkenar Wetland, following by microbeads/spherules.

There was clear dominance of MPs < 250 μm and these had a variety of elements onto them including Fe, Cu and Pd. Hence, mismanagement of waste is contributing to rising concerns about the wetland. There is an urgent need to achieve sustainable and systematic management services such as regular plastic waste collection plans and domestic wastewater treatment systems in areas affecting wetlands. Findings from this study can finally be used by planners and policymakers to improve these vulnerable systems an drespond to increasing inputs of plastic pollution. Therefore, it is recommended that local and governmental institutions organize programs of inhibition of poaching with illegal techniques and make suitable decisions for rice farmers as key stakeholders of the wetland to prevent them from using plastic materials affecting the reservoirs. The findings of this research provide a foundation for further research in the Freidounkenar Wetland that should highlight relationships between the MPs contaminations in different wetland media and during different seasons for instance address the presence and effect of MPs in aquatic organisms. Also, this study may be used to understand the possible association between the high concentrations of metals reported in birds in the wetland with MPs pollution.

CRediT authorship contribution statement

All authors contributed to the study conception and design. **Negar Ashjar**: Investigation, Writing – original draft, Conceptualization, Formal analysis. **Behnam Keshavarzi**: Supervision, Conceptualization, Project administration, Resources, Reviewing and Editing. **Farid Moore**: Supervision, Project administration, Resources, Reviewing and Editing. **Mehdi Zarei**: Investigation, Project administration. **Rosa Busquets**: Reviewing and Editing. **Seyed Mojtaba Zebarjad**: Reviewing and Editing. **Zargham Mohammadi:** Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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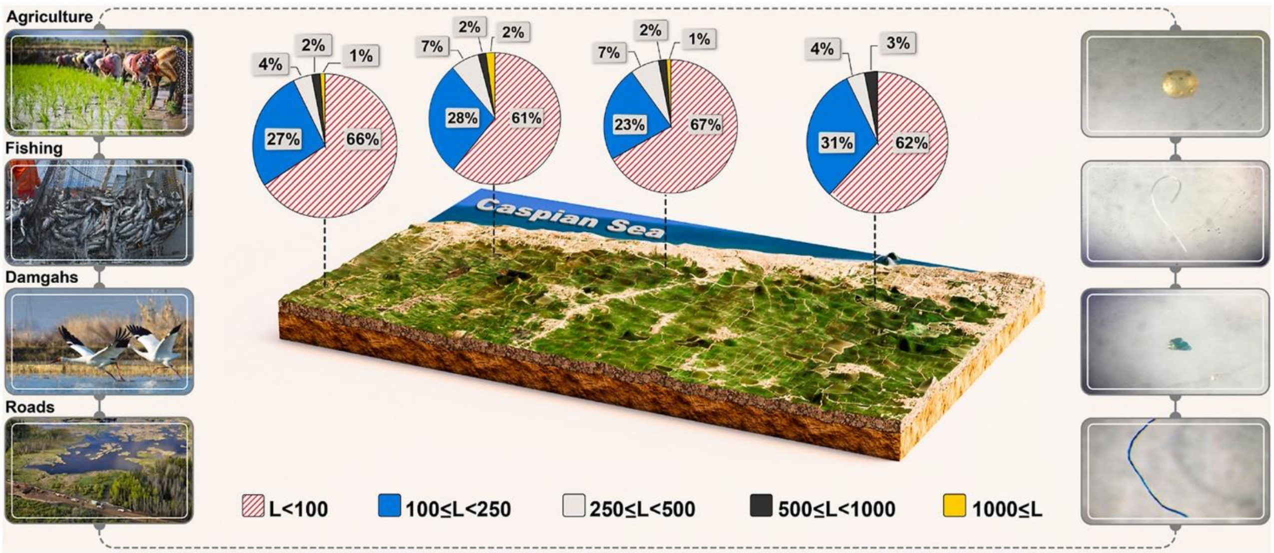
Graphical abstract



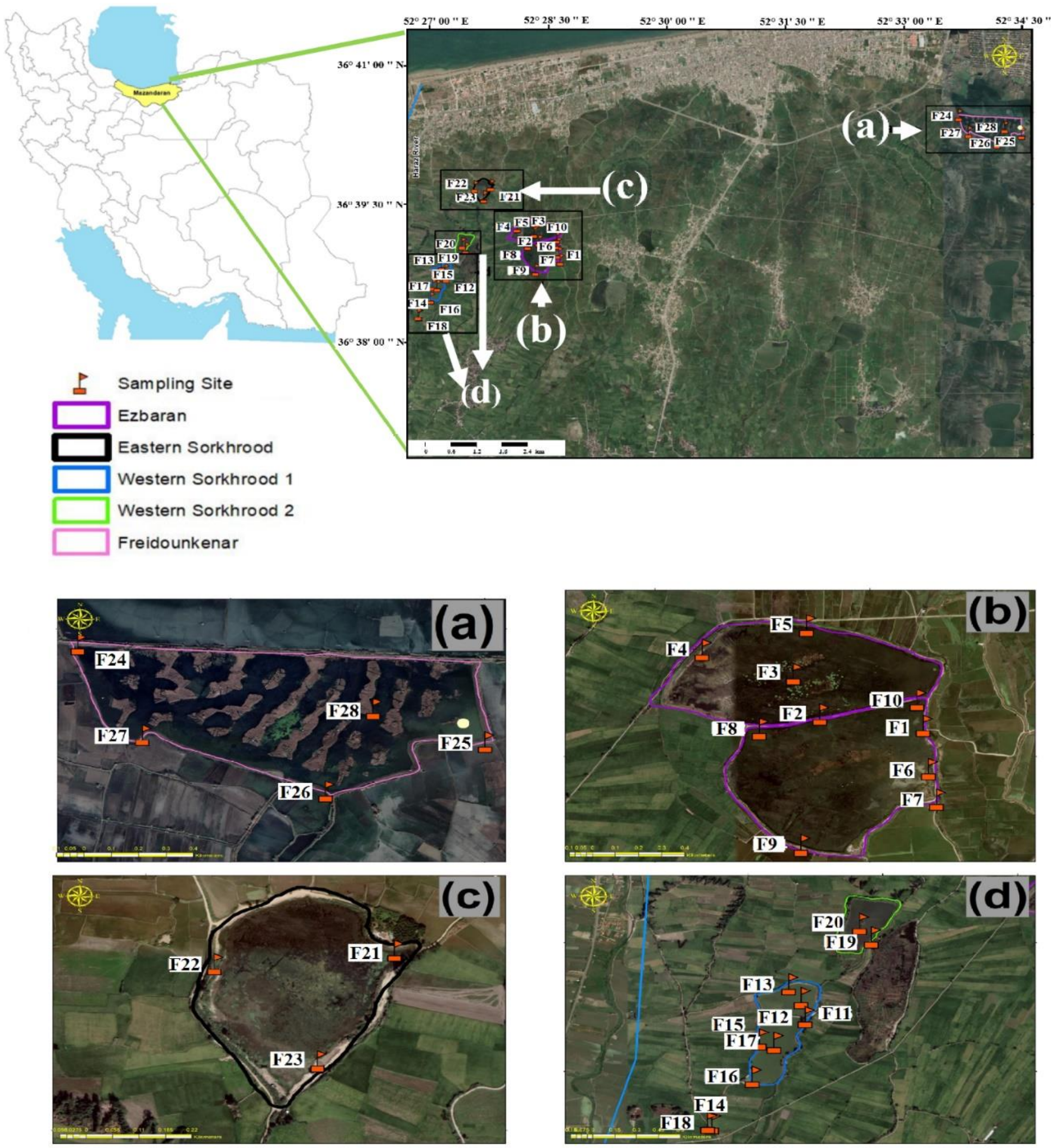


Fig. 1. Locations of sediment samples (F1-F28) in four Ab-bandans of Freidounkenar Wetland: (a) Freidounkenar Ab-bandan, (b) Ezbaran Ab-bandan, (c) Eastern Sorkhrood Ab-bandan, (d) Western Sorkhrood Ab-bandan.

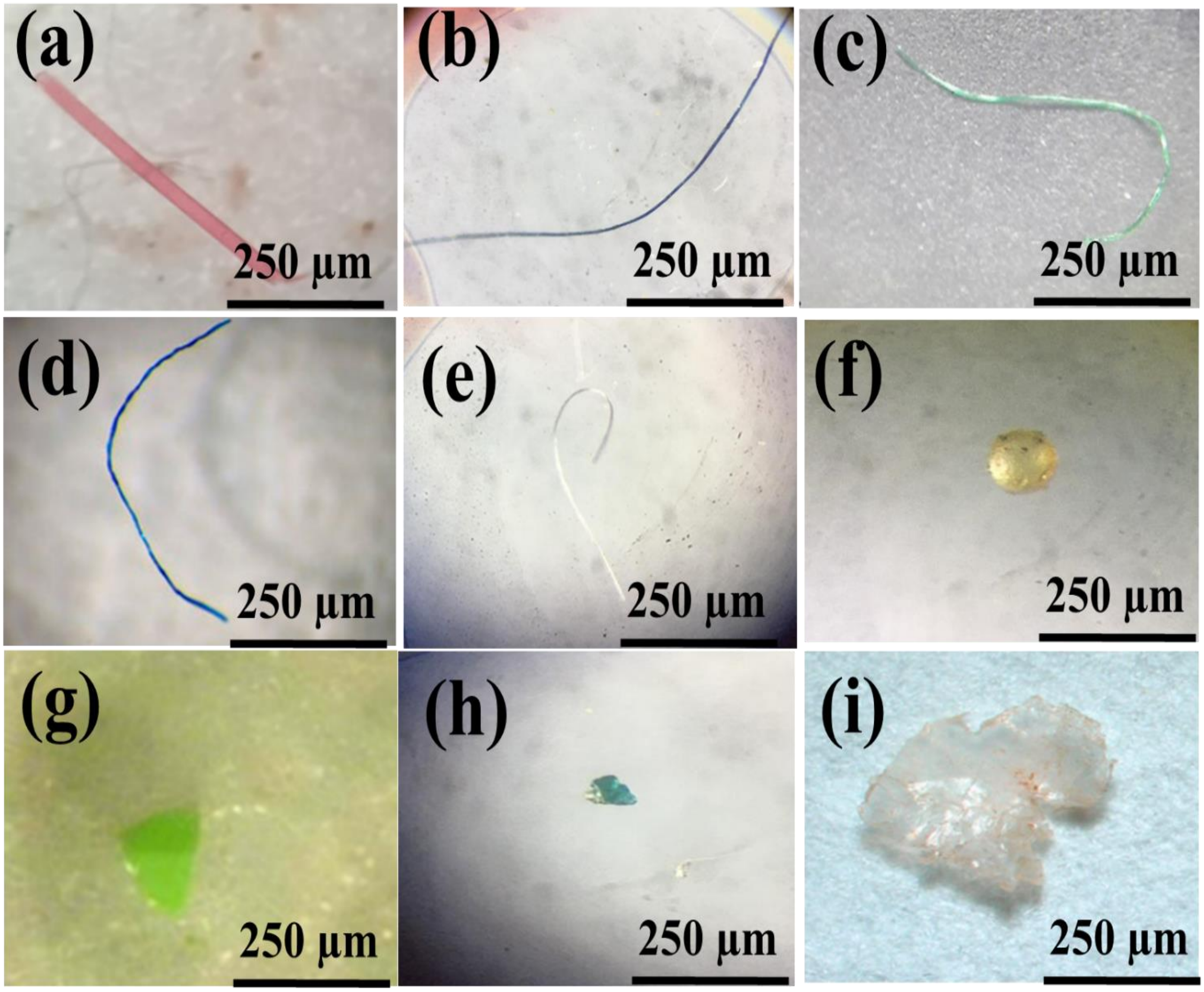


Fig. 2. Representative MPs from wetland sediment observed with an optical microscope. Fibers are shown in a,b,c,d,e; spherule (f); and fragment (g,h,i).

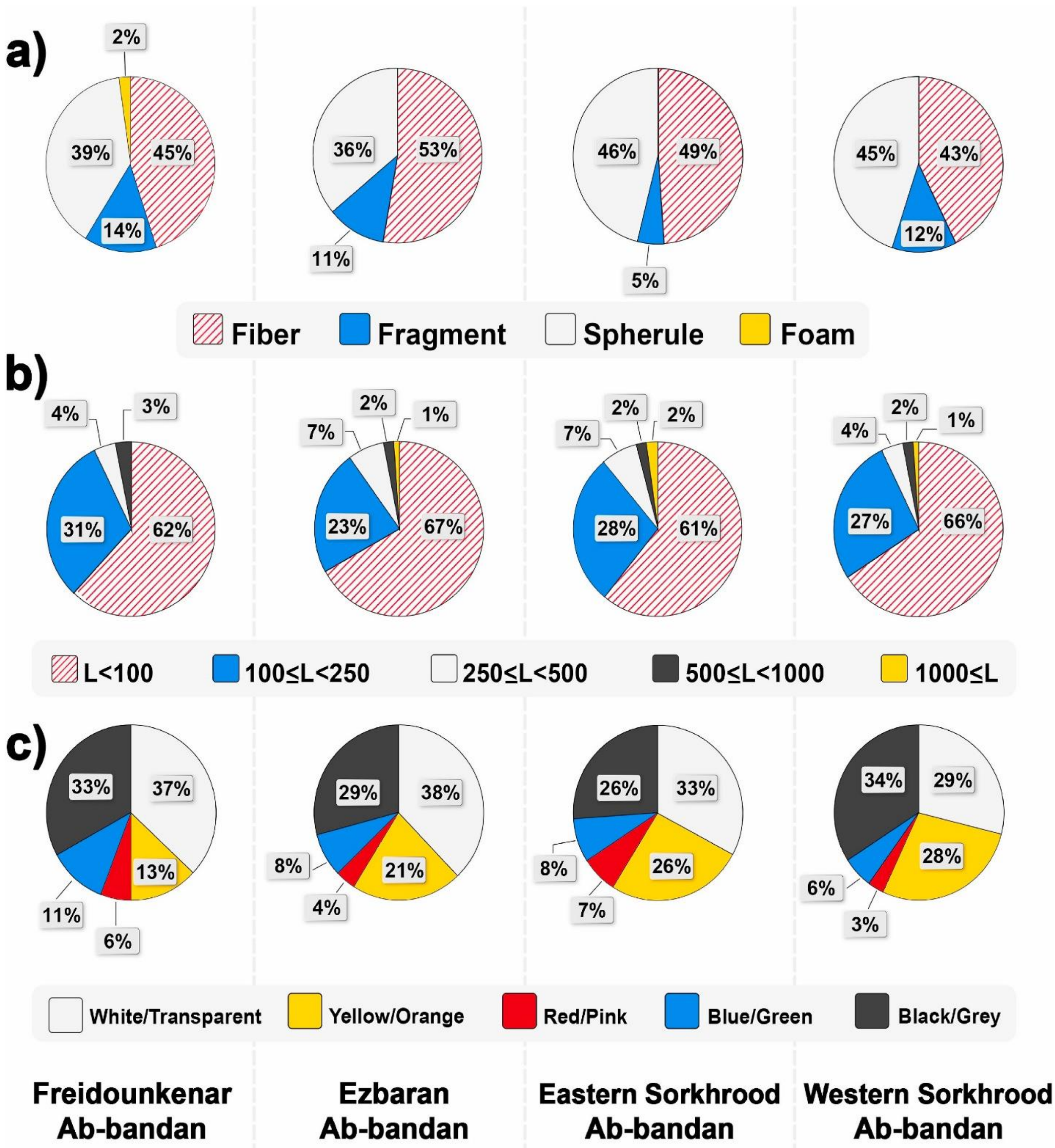


Fig. 3. Distribution of MPs classified by their (a) shapes, (b) sizes (μm) and (c) colours in four Ab-bandans of Freidounkenar Wetland. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

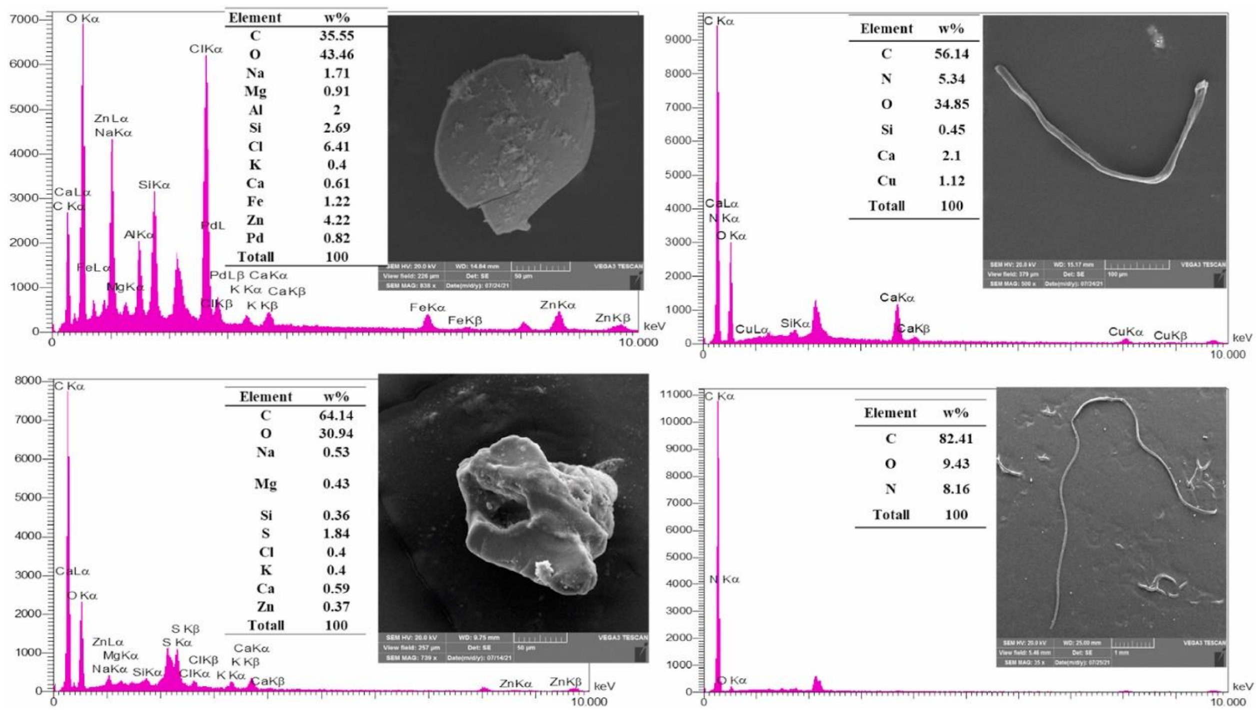


Fig. 4. SEM micrographs with EDX spectra displaying the surface morphology and chemical composition of selected MPs in sediment samples.

Microplastics (MPs) distribution in Surface Sediments of the Freidounkenar Paddy Wetland

Supporting Information S1. Descriptions of Ab-bandan and their role in the the International Freidounkenar Wetland:

Mazandaran is a wet province and a major rice producer in Iran with 37% of land under rice cultivation (Ministry of Agriculture Iran, 2016). There is a traditional water harvesting system in Mazandaran, called Ab-bandan, a man-made water storage reservoirs or artificial wetland, used by local farmers to collect the precipitation and flood during non-growing seasons (autumn and winter), for rice farming and the livelihoods of local people during the growing seasons (spring and summer) (Ghoddousi, 1999; Rahimi Farahani et al., 2012). Ab-bandans are typically constructed by digging the land and compacting the soil to construct a wall around the dugout pond by local farmers. The history of Ab-bandan construction goes back to about 3000 years ago (Ejlali et al., 2012; Ghoddousi, 1999). Generally, these reservoirs do not have any geometrical shapes with different size ranging from 3 to 1000 hectares (Abbasian et al., 2014). The total area of Ab-bandans in Mazandaran province is estimated as 17,000 hectares. Ab-bandans supply 331 million m^3 of water for 51,736 hectares of rice fields in the province which is a considerable amount in comparison to the volume of large dams (304 million m^3) in this area (Mazandaran Regional Water Authority, 2016). Water supply for rice cultivation, collecting drainage water, recharging underground wells, supporting aquaculture and provision of leisure zones are identified as the most important functions of Ab-bandan (Vosoughi and Mohammadi, 2013).

Table S1. Abundance of MPs based on shape, size and colour in sediments (MPs/kg) of the Freidounkenar Wetland.

Sample No.	**UTM**		**Total number**	**Shape**				**Size**					**Colour**				
	X	**Y**		**Fiber**	**Fragment**	**Spherule**	**Foam**	**L < 100**	**100 ≤ L < 250**	**250 ≤ L< 500**	**500 ≤ L < 1000**	**1000 ≤ L**	**White/Transparent**	**Yellow/Orange**	**Red/Pink**	**Blue/Green**	**Black/Grey**
F1	632033	4057201	38	19	3	16	0	27	9	0	2	0	10	6	1	6	15
F2	631673	4057246	39	27	4	8	0	31	4	4	0	0	17	3	2	4	13
F3	631579	4057425	44	35	0	9	0	23	14	4	1	2	19	0	0	1	24
F4	631260	4057528	40	24	8	8	0	37	1	0	1	1	13	3	0	9	15
F5	631621	4057643	76	29	18	29	0	44	29	0	3	0	53	19	0	0	4
F6	632054	4057008	45	36	0	9	0	32	9	3	1	0	14	16	6	1	8
F7	632084	4056872	34	21	0	13	0	27	7	0	0	0	9	9	3	2	11
F8	631464	4057179	86	36	1	49	0	39	30	17	0	0	24	29	1	4	28
F9	631616	4056661	54	23	18	13	0	41	6	3	1	3	19	10	5	9	11
F10	632009	4057316	43	14	2	27	0	31	7	2	2	1	15	9	1	3	15
F11	629917	4056635	24	17	0	7	0	9	12	1	1	1	17	0	0	0	7
F12	629942	4056498	78	24	29	25	0	55	21	1	0	1	34	25	2	2	15
F13	629848	4056732	56	20	8	28	0	46	8	2	0	0	10	22	0	0	24
F14	629439	4055728	48	19	0	29	0	28	17	3	0	0	11	12	0	0	25
F15	629691	4056334	50	16	0	34	0	32	13	5	0	0	9	13	3	2	23
F16	629656	4056063	36	20	0	16	0	25	5	2	3	1	18	8	2	3	5
F17	629773	4056311	29	7	0	22	0	16	12	0	0	1	4	6	0	0	19
F18	629416	4055731	49	38	0	11	0	32	13	2	2	0	11	15	4	8	11
F19	630299	4057077	45	17	14	14	0	33	8	3	1	0	11	12	3	10	9
F20	630232	4057171	23	13	0	10	0	14	8	0	1	0	4	8	0	0	11
F21	630751	4058346	49	23	0	26	0	31	13	1	2	2	20	15	0	1	13
F22	630450	4058313	66	30	7	29	0	43	19	4	0	0	19	16	5	8	18
F23	630626	4058112	41	24	0	17	0	21	11	6	1	2	12	10	6	3	10
F24	639551	4059900	63	44	6	7	6	32	23	4	4	0	49	7	0	1	6
F25	640749	4059552	47	17	0	30	0	31	14	0	1	1	5	8	2	0	32
F26	640285	4059360	54	10	11	33	0	42	12	0	0	0	13	2	3	9	27
F27	639745	4059562	67	36	15	16	0	43	18	5	1	0	22	7	7	16	15
F28	640419	4059672	44	17	5	22	0	23	19	1	1	0	13	12	4	3	12
Sum			1368	656	149	557	6	888	362	73	29	16	475	302	60	105	426
Min			23	7	0	7	0	9	1	0	0	0	4	0	0	0	4
Max			86	44	29	49	6	55	30	17	4	3	53	29	7	16	32
Mean ± SD			49 ± 15.43	23 ± 9.16	5 ± 7.46	20 ± 10.48	0.2 ± 1.13	32 ± 10.32	13 ± 7.06	3 ± 3.35	1 ± 1.07	1 ± 0.83	17 ± 11.55	11 ± 7.1	2 ± 2.18	4 ± 4.09	15 ± 7.47
Median			46	22	2	17	0	32	12	2	1	0	14	10	2	3	14

Table S2. Summary of MP occurrence in sediments (MPs /kg DW) in the study area compared with wetlands elsewhere.

Location	Medium	Abundance MPs/kg	Major polymer	Major shapes	Reference
Anzali Wetland, Iran	Sediment	30 - 1380	PP, PE	Fiber	Birami et al., 2022
Xijin Wetland Park, South China	Sediment	4 - 148	PET, PE	Fiber	Wang et al., 2021
Hashilan Wetland, Iran	Sediment	0 - 8	PP, PS, PE	Fiber	Abbasi et al., 2021
Anzali Wetland, Iran	Sediment	140 – 2820 n/kg (June), 110 – 3690 (January)	PP, PE , PET	Fiber, Fragment, Film	Rasta et al., 2020
Western Norway	Sediment	12000 - 200000	NY	Fiber	Haave et al., 2019
Poyang Lake, China	Sediment	54 - 506	PP, PE	Fiber	Yuan et al., 2019
Mangrove wetlands, China	Sediment	15 – 12852	PP, PS, PE	Fragment	Li et al., 2018
Southern coasts of the Caspian Sea, Mazandaran, Iran	Sediment	25 – 330	PS, PE	Fiber	Mehdinia et al., 2020
Freidounkenar Wetland, Iran	Sediment	23 – 86	NY, PP, PS, PE	Fiber	This study

PP: polypropylene, PE: polyethylene, PET: polyethylene terephthalate, PS: polystyrene, NY: nylon

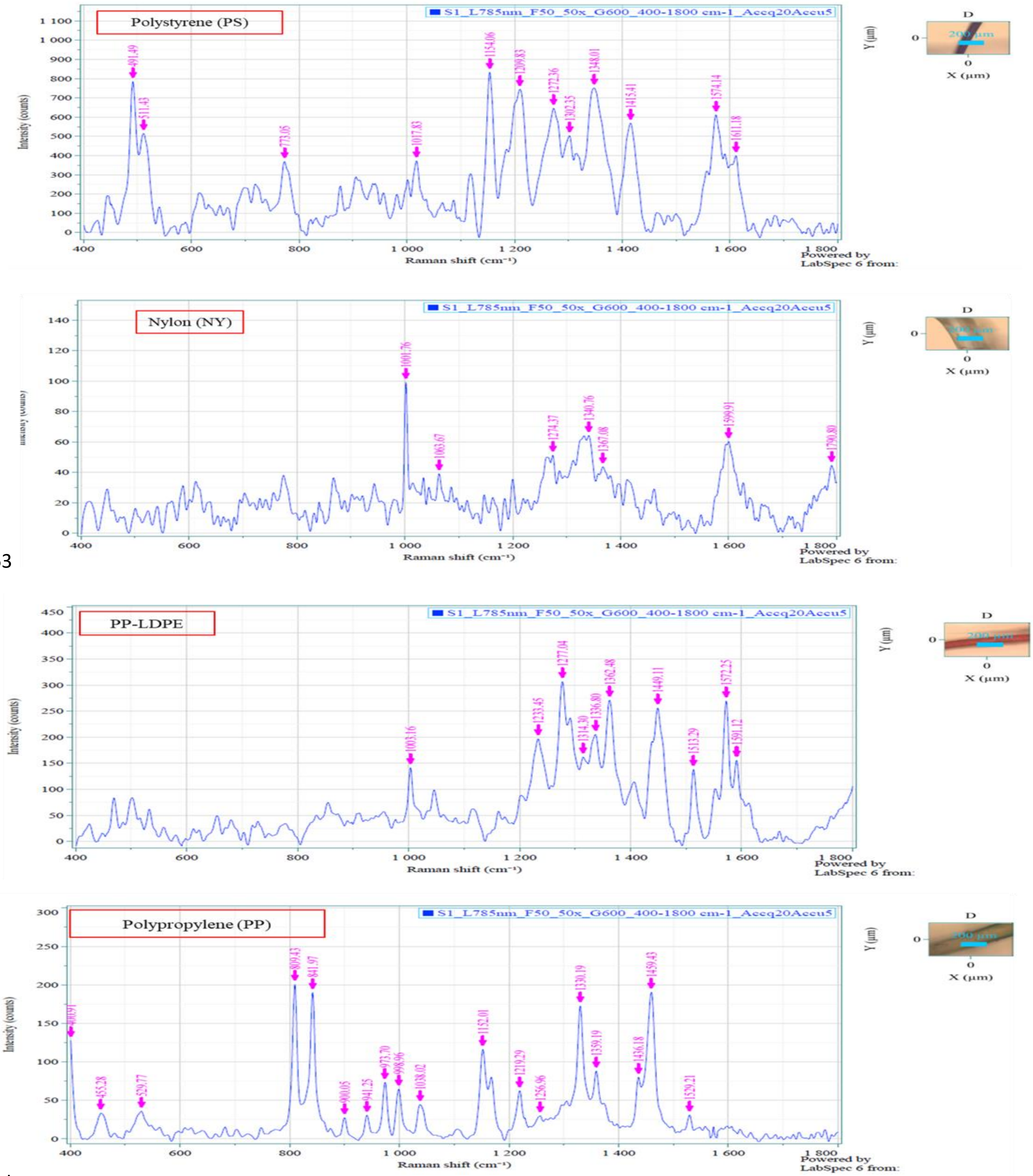


Fig. S1. Raman spectra of four representative MPs showing main polymers making them up.

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