Research Paper Microplastics and Microrubbers in Soils Around Two Landfills and a Municipal Solid Waste Transfer Station in Ahvaz Metropolis, Iran

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ABSTRACT

Background: Microplastics (MPs) and microrubbers (MRs) are a substantial source of pollutants entering the environment and a cause for debate in environmental studies in soils surrounding two landfills and a municipal solid waste transfer station near Ahvaz Metropolis. Since the current information about these particles in Iranian municipal solid waste transfer station and landfill systems is scanty, this study aimed to determine the amounts and abundance of MPs and MRs in soils.

Methods: Each of the twelve sites that determined using a systematic grid sampling method had approximately 100 g of soil samples from a depth of 0-10 cm with three replications. The method used for extracting MPs from the soil samples was density separation with saturated zinc chloride solution. The particles were investigated by the size, shape, abundance and colour. A total of 1807 MP and 1872.7 MR particles were detected from the samples. The Pearson's correlation coefficient (r) was used for describing correlations.

Results: The highest abundance of MPs was observed at the S5 site $(325.9\pm26.8 \text{ items}/100 \text{ g} \text{ soil})$. The particles were categorized into fragments, foams, fibers, films and spheres. Five ranges of particle size were identified (between 1 mm \leq L and L \leq 100 µm) in nine color categories. The 1 mm \leq L size class was dominant in MPs (54%) and MRs (52%). The majority of the MPs (41.8%) were white/transparent, whereas MRs were identified as black/gray (99.1%).

Conclusion: Contamination by MPs and MRs exceeded allowable standards, compared to other transfer stations across the globe.

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1. Introduction

icroplastics (MPs) are an emerging group of pollutants that exist in different environmental media. Due to their wide range and potential environmental hazards, they have attracted widespread attention in recent years. At

present, research on MPs is focused mostly on aquatic ecosystems, whereas their impact on soil ecosystems has less been studied [1]. MPs are heterogeneously-mixed plastics that are less than 5 mm in diameter and include plastic fibers, granules and fragments. They can be divided into either primary MPs (directly produced MPs) or secondary MPs (resulting from macroplastic fragmentation). Microrubbers (MRs) are a type of MPs that are distinctly different in terms of their appearance, physical properties, deformation characteristics, sources and uses [2]. There is no doubt that the best way to eliminate MP pollution is to control and prevent plastics from entering the environment. Strategies for controlling them have been indicated by several sources; hence, it is of great importance to understand the sources and pathways that lead MPs to entering the environment [3].

A major release of MPs to the environment is generally recognized as a result of inappropriate waste management and improper human behavior [4]. Among these, one of the waste management stages is landfilling which should be regarded as an important MPs entry source. Landfills are receptacles for cumulative loading of plastic wastes derived from industrial and household sources, but data on the occurrence of MPs in landfill systems remain insufficient [5]. Landfills are home to 21%-42% of global plastic waste production. The rest is carelessly released into the environment because of mismanagement, accidental disposal or the mishandling of plastics and their wastes. Furthermore, landfills are sometimes mismanaged by not having fences surrounding them, accompanied by inappropriate types of synthetic material that should otherwise cover wastes thoroughly (Duis and Coors). Nonetheless, MPs enter the environment through a variety of pathways. Landfills are largely suspected to release MPs into the environment, although few cases of empirical research have been carried out on this field to date [6].

Once in the soil, MP accumulation may cause a series of adverse effects on soil ecosystems. MPs affect soil physical and chemical properties, microbial and enzyme activities and plant growth. Also, they pose adverse ecotoxicological threats to the soil fauna [7]. These effects depend on the concentration, size, and shape of MPs, as well as soil texture. MPs are known to absorb organic and inorganic pollutants, possibly affecting the distribution of these substances in the soil. The horizontal and vertical transport of MPs can be facilitated by the soil fauna. Pollutants associated with soil fauna may dissipate further, following the dispersion of them in soil [8].

Plastic pollutants were first recognized on a large scale in marine environments [4]. Over the past 10 years, many studies have investigated the distribution and effects of MPs within the category of plastic pollution. However, few studies have aimed at evaluating landbased sources of MPs [1]. It should be pointed out that soil may represent a direct, major sink of MPs [9]. It is estimated that the amount of plastics released annually into the terrestrial environment is 4-23-fold greater than that released into the marine environment [10]. Recently, several studies have assessed MP contamination in soils. This type of pollution was first addressed by Rillig [10] and, since then, an increasing number of studies have focused on this crucial matter [11, 12]. The presence and distribution of MPs have lately been studied in some landfills. Specifically, Puthcharoen et al. [13] examined MPs in soil and in leachate samples obtained from landfill sites located around the Gulf of Thailand. These were analyzed by using the density separation technique. Usually, Fourier transform infrared spectroscopy (FTIR) enables a close analysis on MPs from which five specific plastic shapes are identified, i.e. fibers, films, spheres, granules and irregular shapes. He et al. [6] investigated evidence for MPs in landfill leachate at six municipal solid waste (MSW) landfills from four different cities in China (Shanghai, Wuxi, Suzhou and Changzhou). The researchers used the FTIR spectrometer for this purpose. Su et al. [5] evaluated the distribution pattern of MPs in landfills (including leachate) of Shanghai, as a megacity, in accordance with different landfill ages- 3-20 years. Van Praagh et al. [14] did research on the occurrence of MPs (5000-50 µm) in leachates of 11 landfills in Finland, Iceland and Norway using the FT-IR spectroscopy.

Ahvaz is a large metropolitan city in Iran. Its rapid increase in solid waste production reflects fast population growth, urbanization, rapid industrialization and economic development. According to the statistics reported by the Ahvaz waste management organization (AWMO), only 305,140 tons of waste were generated in this metropolis in 2019. Almost a tenth of this amount (9.42%) comprised plastic materials [10].

The aims of this research were to investigate MRs in Ahvaz for the first time. The presence of MPs was explored in soils surrounding two landfills and a MSW transfer station. The radius covered 200 meters of the approved area for each site. The average abundance and size of MPs and MRs were estimated according to their morphological characteristics such as color, shape, size and abundance. Also, the MSW transfer station and landfill were evaluated as tow sources of MPs and MRs, which infected the environment.

Other studies have rarely determined the presence of MPs and MRs in landfills and MSW transfer stations. Therefore, a vast amount of research on the occurrence of MPs, MRs and specific features of the pollution is vital in these system.

Previous research in this field led us to believe, all necessary information was reviewed in relation to sampling techniques, separation, density extraction, identification by different microscopes and how to ascertain them with the standard methods and protocols, according to the available literature.

Problems with this study were the lack of specific standards for sampling, separation, characterization and analysis of MP materials in solid, liquid or even gaseous matrices, time-consuming techniques, scarcity of equipment and high cost. Measurements of contaminants adhering to their surfaces may lead to inadequate comparison of data and possibly uncertain conclusions; thus, a literature review revealed that that different researchers tend to resort to different strategies in this regard.

We evaluated the occurrence and characteristics of MPs and MRs for the first time in soils surrounding two

MSW landfills and a MSW transfer station in Ahvaz Metropolis, Iran. We discussed how these two locations can be potential sources of MPs and MRs. Since the available literature on these two is not fully developed in waste management throughout the world, some aspects of this research can serve as a point of comparison and reference for future research elsewhere. The novation of this research involved evaluating MPs and MRs in soils around MSW Transfer Station that had not been studied before. It thought of MPs and MRs using a particular method for the first time in Ahvaz.

2. Materials and Methods

Study area and sampling site

Ahvaz is one of the largest cities in Iran. It is the capital of Khuzestan Province and is located in the southwest of Iran, between 48° 40' E and 31° 20' N, with an area of 220 k (Figure 1). According to the United Nations World Population Prospects, 1,228,000 people live in Ahvaz [15] among 286032 households. It also includes eight municipality districts [16]. The total amount of solid waste being generated in Ahvaz is about 305,140 tons/ year [10]. Three sampling sites were selected (shown in Figure 1). The first site was an active sanitary landfill (Safireh), located 25 km southeast of Ahvaz. It receives about 1300 tons of municipal solid waste a day. The "Fukuoka Method" (semi-aerobic landfill) is the main method of MSW disposal in the Safireh landfill [10]. The second site was a closed traditional landfill, located in the Boromi region, 10 km from the city. In this site, wastes were disposed of by means of traditional meth-

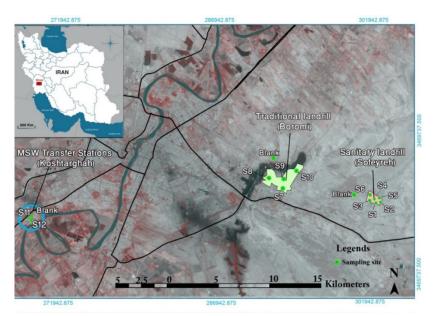


Figure 1. Location of the study area and distribution of sampling sites in Ahvaz metropolis

ods. Here, modern sanitary techniques such as leachate collection systems and impermeable linear layers were absent. The third site, the MSW transfer station (Ahvaz slaughter house), was located near a slaughterhouse, 15 km away from the Ahvaz-KhorramShahr road and near Karun River [10]. Information about locations and the description of sampling sites have been listed in Table 1.

Sample collection of MPs and MRs

The soil samples were collected in January, 2020, from around 12 sampling sites. The sampling area was within a 200-meter radius of the approved location for each site. The samples were collected from a depth of 0–10 cm (Figure 1) by applying the 'systematic grid sampling' procedure. In three replicates, about 100 g of soil per sample was collected from each sampling site using a stainless steel shovel. Then they were kept in glass jars and transferred to the laboratory for further assays [14]. The soil samples were air-dried at room temperature (20-25°C) and then passed through a sieve with 5 mm openings. Finally, these samples were used for analyzing soil texture, pH and electrical conductivity.

Sample preparation

Since the presence of organic materials (e.g. proteins, fats, hydrocarbons, etc.) can interfere with the counting of MPs and MRs, organic materials and organic debris were removed from the surface of the samples. For this purpose, 10 g of each sample was air-dried and sieved with 5-mm metallic mesh [14]. Next, each sample was weighed and mixed with 35 mL H_2O_2 (30%) for 7 days. The addition of H_2O_2 promoted reactivity and the forma-

Table 1. Locations and description of the sampling sites

tion of bubbles that lasted continuously until the seventh day. The samples were then vacuum-filtered through S&S filter paper (blue band, grade 589/3, 2 μ m pore size) and washed using deionized water to eliminate the remaining amount of H₂O₂ on soil particles. The samples were dried in a sand bath at 50°C for 8 hours [17].

Extraction of MPs and MRs

The method of density separation with saturated ZnCl₂ (1.19 g/cm³) solution was used for extracting MPs from the soil samples according to Abbasi et al. method [18]. In each sampling site, three soil samples were evenly mixed for further treatment and assay. The samples were dried at 70°C for 24 h, and then moved into a clean glass beaker. To prepare the ZnCl₂ solution, 1120±0.5 g of powdered anhydrous Zncl₂ (Sigma Aldrich, ACS reagent grade $\geq 97\%$) was dissolved in 700±0.5 mL deionized water through an extreme exothermic reaction. Its volume increased to 1050 mL. The solution was gently shaken and, after cooling down to room temperature, it was filtered through an S&S filter paper (blueband, grade 589/3, 2 µm poresize) to remove undissolved salt minerals and impurities [18]. One hundred milliliters of prepared ZnCl₂ solution was mixed with each soil sample and shaken for at least 5 min to separate the particles that stuck together. Afterwards, the samples were left intact overnight. The supernatant, which included floating MP particles, was poured onto filter papers gently and the ZnCl₂ solution was recycled by pressure filtration and was used for the next separation step for the same sample [17]. Filter papers were air-dried for 24

Sample Sites	Longitude Latitude (DMS)	status	Topography Type	Area (ha)	Disposal Capacity) Ton/day)	Type of Waste	Landfill class	Operation Time	Sample No.	Sampling Date
Sanitary landfill (So- feireh)	31° 17'15.36" N 48° 5513.44" E	Active	Plain	125	1300	MSW	Non-haz- ardous	2011~ now	S1, S2, S3, S4, S5, S6	04/01/2020
Traditional landfill (Boromi)	31° 18′7.2″ N 48° 48′44.64″ E	Closed	Plain	500	1250	MSW	Non-haz- ardous	2011- 1988	S7, S8, S9, S10	05/01/2020
MSW transfer station (Ahvaz Slaughterhouse)	31° 15'42.83" N 48° 34'08.55" E	Active	Plain	0.7	400	MSW	_	2002 ~ now	S11, S12	06/01/2020

h. MPs were transferred to glass petri dishes using a clean non-plastic brush [19].

Identification and characterization of MPs and MRs

The MP particles in each extracted sample were visually and microscopically identified and separated using tweezers, according to the criteria proposed. Optical microscopy was initially used to help assess extraction techniques and also as the first step in plastic screening in all samples [10]. MPs and MRs were observed by a stereomicroscope (Optika SZM-LED2) under ×10 magnification and binocular polarization microscopy with up to ×200 magnification (Olympus XSZ-801 BN). Images were obtained with a digital camera (Olympus SZX16) [2, 17]. The extracted MPs and MRs particles were counted using a stereomicroscope/binocular polarization microscope. Particle size was measured using Eye Piece Micrometer and Stage Micrometer slides while in microscopic view. This approach is based on the use of an ocular micrometer allowing to take measurements on the MP particles, observed by a microscope. An ocular micrometer is a glass disc acting as a ruler on which a series of uniformly spaced lines (with 0.01 mm or 10 µm divisions) are inscribed. To take a measurement, the ocular micrometer was placed on eyepieces of the microscope and calibrated against the stage micrometer. For calibration, the ocular and stage micrometer were superimposed, and the number of ocular lines per stage micrometer was determined. Accordingly, the diameter of the field of view was used as a scale. We then placed the observed particle so that the eye micrometer could measure the length of particle in the desired units. Optical microscopy was used as a pre-screening technique to reduce the number of particles that needed to be analyzed by scanning electron microscopy (SEM) [11]. Though visual sorting and identification is feasible for large MPs with disguisable color or morphologies, particles without identifiable color or shape are processed with difficulty for visual sorting with the naked eye. Thus, electron microscopy is essential for identifying ambiguous plastic-like particles [20].

SEM was accompanied with energy dispersive X-ray spectroscopy (SEM-EDS). The images were used for characterizing the morphology of ultra-small individual MPs, selected by optical microscopy, and for determining their elemental compositions [1, 3, 20]. Prior to the analysis, most of the loosely adhered materials were removed from the surface of MPs after ultrasonic cleaning. After ultrasonic cleaning, all samples were mounted onto double-sided adhesive carbon tabs on aluminum SEM stubs. SEM/EDS analyses were conducted using an Environmental SEM (FEI ESEM Quanta 200, USA) and a EDS System (EDAX EDS Silicon Drift 2017). The samples were coated with a thin film of platinum, and then imaged using a field emission SEM operating at 20 keV, (50X–10,000X) using the SEM's back-scattered electron (BSE) detector. SEM/EDS provided high resolution imaging of particle surface structures, as well as elemental composition signatures. This information was used for screening possible MPs and to rule out non-plastics.

Next, MPs and MRs were classified according to their morphological characteristics. In terms of color, the classifications included white-transparent, yellow-orange, red-pink, blue-green, black-grey and other. Regarding shape, they were classified as fragments, films, fibers, foams and spheres. Based on size and in terms of length or primary diameter, they were categorized as very long (1 mm \leq L), long (500 µm \leq L<1 mm), medium (250 µm \leq L<500 µm), short (100 µm \leq L<250 µm) and very short (L \leq 100 µm) [21]. MRs are characterized generally by a distinct non-gloss black appearance, high elasticity and structural resilience [17, 18].

Physicochemical parameters of soil

Standard methods were used for analyzing soil texture, pH and electrical conductivity (EC). Soil texture analysis was performed after obtaining the results of hydrometer tests through the ASTM D422-63 method [3]. To determine the pH and EC of the soil, a pH-meter was used according to the ASTM D4972-19 standard test method. A conductivity meter (Inolab-IDS Multi 9310) was operated in the presence of a soil-to-water ratio of 1:5 [20].

Data analysis

Quantitative data were presented as Mean±SD when describing the size, shape, color, abundance and physicochemical parameters of the soil' MPs and MRs. MPs and MRs in the soils were reported per gram of sample. Significant differences in MPP abundance among different sampling sites were determined by a one-way analysis of variance (ANOVA) test, with a post hoc Tukey test. The non-parametric KolmogorovSmirnov test was used for checking whether the data were normally distributed. The Pearson's correlation coefficient (r) is generally used for finding correlations among relationships that connect variables. Also, the coefficient was used for describing correlations between the abundance of MPs, MRs and physicochemical properties of the soil. Statistical analysis was carried out using the SPSS software, version 20 (IBM,

USA). The geographic locations were portrayed by ArcGIS (10.6, Esri, USA).

3. Results and Discussion

Physicochemical parameters of the soil samples

The physicochemical characteristics of the soil samples have been shown in Table 2. The pH values of soil samples were consistently high at the different sites, although with variations, ranging from 7.7 ± 0.05 at S1 to 8.9 ± 0.0 at S9. The electrical conductivity (EC) of the samples from different sites ranged from 2.26 ± 0.01 dS/m at S1 to 8.29 ± 0.05 dS/m at S2, indicating a difference in soil composition at the different sites. Generally, no significant difference occurred in the correlation between the abundance of MPs and MRs, and between pH and EC values of the soil.

Ultimately, two texture groups were found. The first was silty clay which comprised 11.32% sand, 37.34% silt and 51.29% clay in the sanitary Sofeireh landfill and, separately, 9.33% sand, 49.28% silt and 41.38% clay in the traditional Boromi Landfill. Second, a soil texture of silty clay-loam was found which comprised 5.73% sand,

63.4% silt and 31.12% clay in the MSW Transfer Station near the Ahvaz Slaughterhouse (Table 2). The results of correlation analysis between the abundance of MPs and MRs showed no significant difference.

The difference among physicochemical characteristics of the soil samples were perhaps due to the import of soil from outside of the facility. Soil is often used for covering landfills or for extinguishing unexpected fires.

Abundance of MPs and MRs in the soil samples

The results indicated the presence of MPs and MRs in all stations of the study area, but none of which were detected in the blank samples and in the control petri dishes (Figure 2G). A total amount of 1807 MPs and 1872.7 MRs particles were detected in 12 soil samples. Previous results on a case of MPs in landfill soil located around the Gulf of Thailand indicated the presence of 1457.99±489.71 (items per Kg) of soil [13] showing fewer particles than those observed in this study. Figures 3D and 4 d showed the abundance of MPs and MRs in all the soil samples. The highest abundances of MPs were observed at sites S5 (325.9±26.8 items per 100g soil), followed by S2 (226.9±17.3 items per 100

Table 2. Selected physicochemical properties of the soils in each sampling site

Sample No.	Soil Classification	Sand (%)	Silt (%)	Clay (%)	рН	EC (dS/m)
\$1	sic	11.26	38.08	50.66	7.7±0.05	6.26±0.01
S2	sic	10.02	36.28	53.7	8.7±0.01	7.29±0.05
S3	sic	12.42	38.57	49.01	8.8±0.05	6.93±0.02
S4	sic	11.27	37.09	51.64	8.3±0.00	7.18±0.00
S5	sic	11.98	37.12	50.9	8.7±0.01	6.37±0.01
S6	sic	10.98	36.9	52.12	8.6±0.00	6.20±0.00
Blank	sic	11.17	36.71	51.99	8.8±0.00	6.91±0.00
S7	sic	9.43	49.6	40.97	8.5±0.00	4.57±0.02
S8	sic	10.39	48.6	41.01	8.5±0.01	5.14±0.00
S9	sic	8.01	48.79	43.2	8.9±0.00	5.53±0.03
S10	sic	9.5	50.14	40.36	8.8±0.05	4.51±0.01
Blank	sic	10.06	48.14	41.80	8.9±0.01	4.92±0.00
S11	sicl	4.48	64.4	31.12	8.3±0.0.3	3.52±0.05
S12	sicl	6.98	62.25	30.77	8.4±0.00	3.43±0.02
Blank	sicl	6.25	62.8	30.95	8.1±0.01	3.81±0.00

Abbreviations: Sic: Silty clay; Sicl: Silty clay loam; EC: Electric conductivity



Figure 2. Binocular microscopic images of different types of MPs and MRs (A) Fragmented MPs; (B) Films MPs; (C) Fibrous MPs; (D) Foam MPs; (E) Sphere MPs; (F) Fragmented MRs; (G) Blank sample.

g soil) within the sanitary Sofeireh landfill. These two stations are located near younger landfill cells without surface cover systems, as compared to medium and old landfill cells (P<0.05), thereby spreading plastic debris in the surrounding environment. The amount of MPs and MRs were found to increase with a lin-

ear relationship. The lowest amounts in S6 (65 \pm 4.5), S7 (100.4 \pm 7.6) and S12 (122.4 \pm 8.01) stations were found far from the younger landfill cells. The highest abundance of MRs was found in S12 (829.3 \pm 123.5 items/100 g soil) and S11 (205.5 \pm 47.6 items/100 g soil) in the MSW transfer station (Ahvaz Slaughter-

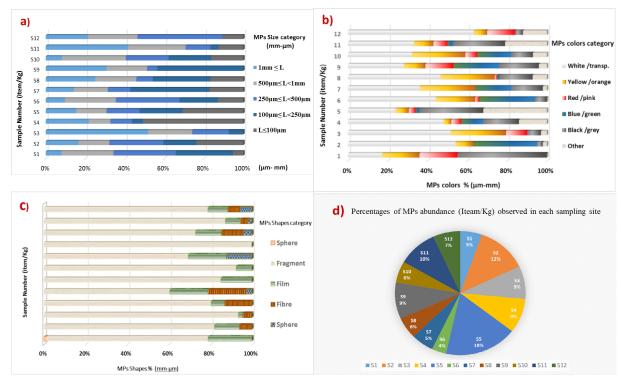


Figure 3. Proportions of each A) Size; B) Shape; C) Color category; D) Abundance percentages of MPs

house). These high amounts could be explained by the local proximity to road traffic [21] and garbage trucks. The samples S9 (17.6 \pm 4.9 items/100 g soil) and S6 (21.5 \pm 3.3 items/100 g soil) of the MRs in the traditional and sanitary landfills, respectively, exhibited the lowest abundance in comparison with other sites. A relative standard deviation of the counted number of MPs and MRs showed values of 71.4 and 222.6, respectively, indicating a high heterogeneity among soil samples. However, a nonparametric Kolmogorov–Smirnov test revealed no significant difference between the abundance of MPs and MRs among individual sampling stations.

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Most MPs are usually generated by the fragmentation of macroplastics [5]. The amount of plastic waste entering the MSW transfer station and landfill can affect the abundance of MPs. Given the current method of waste collection and disposal system, landfills receive trash from a vast majority of households and industrial locations, thereby becoming a primary reservoir of MPs [5].

Size and morphology of MPs and MRs in the soils sample

Figures 3 and 4 show the size, shape and color classifications of MPs and MRs in all the soil samples. The size of MPs and MRs particles ranged from less than 1 μ m to 5 mm (Figure 3A and 4A). The first size class (1

mm \leq L) was dominant in most samples. More than 54% of the total MP particles and 52% of MRs were larger than 1 mm. The smallest MPs were between 100 µm and 250 µm, while the smallest MRs were less than 100 μm. In contrast, smaller MPs (<50 μm in size) could remain undetected under the light microscope [21]. The MP abundance showed significant positive correlations with size class. The abundance of 1 mm \leq L and L \leq 100 µm showed correlation coefficients of r=0.737 and r=0.741, respectively (P<0.01). The abundance of MPs (250 μ m \leq L \leq 500 μ m) also correlated positively with the total number of MPs (r=0.584 and P<0.05). Size is very important when considering organisms that may potentially ingest the MPs and how plastic debris may absorb organic pollutants. Smaller MPs can be ingested easier by a wider range of organisms and their bioaccumulation potential also increases [6].

MPs occurred in five shapes in the study area. These were fragments, films, fibers, foams and spheres. In contrast, MRs occurred as fragments only (Figure 2). In general, the distribution of the types of MPs varied at each sampling site. The shapes of MPs are not irrelevant to the source of plastic goods in MSW. MPs were dominated by fragments (53.2%) as one of the major MP morphologies in soil samples. Fragments could be from plastic containers, e.g. bottles of water and food storage containers. Films were the second most common type of particles found (38.1%) to which household plastic pack-

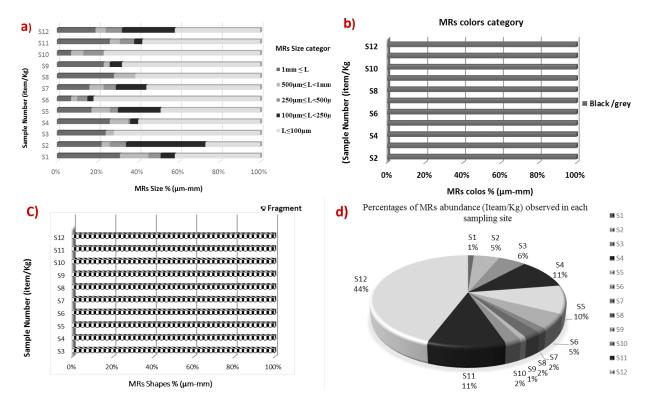


Figure 4. Percentages of A) Size; B) Shape; C) Color category; D) Abundance of MRs in each sampling site

ing and waste bags are probably the primary contributors. The highest quantity of MP fragments was found in stations S3 (88%) of the sanitary landfill and S9 (72%) in the traditional landfill. The highest amount of MP films was found in stations S7 (61%) in the traditional landfill and S11 (48%) in the MSW transfer station. The lowest amounts of MP spheres and foams were (1.6%) and (3%). These are especially thin and transparent in structure which makes them easily breakable when exposed to the sun [13].

The distributions of the different types of MP particles varied at each sampling site. Using Pearson's correlation, an analysis was carried out on the relationship between the total abundance of MPs in general and in different shapes. MP abundance showed significant, positive correlations among fragments, films and foams (r=0.963, r=0.709 and r=0.835, respectively) (P<0.01). The abundance of MP fibers correlated positively with the total number of MPs (r=0.614, P<0.05) which implied that the particles increase in number in a linear relationship. In contrast, no significant correlation was found between the abundance of total MPs and the abundance of spheres. Fragments comprised the largest number of MRs (92.3%). The largest pieces were found in stations S12 (829.3±123.5 items/100 g soil) and in S11 (52.6±7.02 items/100 g soil) in the MSW Transfer Station (Ahvaz slaughterhouse), respectively. The abundance of MRs could be traced to tire rubber in vehicles and garbage trucks. The least amount of pieces was found in S9 (17.6 \pm 4.9 items/100 g soil) and in S6 (21.5 \pm 3.3 items/100 g soil). The abundance of MRs showed a significant, positive correlation with fragment numbers (r=1.00) (P<0.01).

Regarding color classification, MPs were mostly white/transparent (41.8%), followed by yellow/orange (13.64%), red/pink (8.78%), blue/green (13.2%), black/gray (13.9%) and other colors (12.3%) (Figure 3B). On the other hand, MRs were mostly defined as black/gray (99.1%) (Figure 3B). In MPs, 41% of the white-colored particles were fragments. Small and colored MPs are viewed as an environmental threat as they look like edible items to fauna and birds [3, 17]. Despite these observations, however, the nonparametric Kolmogorov–Smirnov test revealed a normal distribution of different sizes, shapes and colors of MPs and MRs among individual sampling stations.

Surface morphological characteristics of the detected MPs and MRs

SEM was a useful screening tool for providing high resolution imaging and observation on the surface textures and morphology of the MP and MR debris. In total, 72 images were obtained from six samples. This information can be applied when screening for probable MRs and MPs and rule out non-plastics. Since high-density polymers can be present in the environment, all settled fragments that physically resembled plastic materials were counted as suspected MPs and were analyzed for chemical composition. The six shapes of MRs and MPs exhibited different weathering morphologies. The SEM images (Figure 5) indicated different degrees of roughness on the surface, along with signs of degradation, including cracks and pitting on the MRs and MPs fragments. These surface features can alter the ability of particles to absorb other materials.

The images of the surface characteristics of MPs illustrate that fragment shapes had a rather smooth surface with no fracturing, despite evidence of mechanical and chemical weathering in the form of flakes and the presence of pits, grooves and irregular edges (Figure 5A). Most film shapes had a highly deformed margin and exhibited a very rough surface (Figure 5B). The surface of the fiber was either concave or convex and, based on partially enlarged pictures, the surface had more scratches than pores and protrusions (Figure 5C). The foam shape was characterized by roughness and a damaged surface (Figure 5D). The sphere had smooth silicate glass surfaces, with a flaking appearance and a bright glow (Figure 5E). The fragmented MRs illustrated a high level of roughness, a damaged surface morphology and microholes (Figure 5F). In general, the MRs and MPs in the soil samples showed weathering features of a rough surface, ragged edges and obvious pores. The ability of MRs and MPs to adsorb pollutants would usually depend on physicochemical properties, such as hydrophobicity and smoothness on their surface.

Analysis of the elemental composition signatures of the detected MPs and MRs

The spectra of the SEM analysis (Figure 5) demonstrated the presence of multiple types of metal elements on the surface of MPs and MRs such as carbon (C), oxygen (O) and trace amount of silicon (Si), aluminum (Al), magnesium (Mg), sodium (Na), calcium (Ca), zinc (Zn) and mercury (Hg). These were indications of additives in plastic polymers or resembled the adsorbed debris on the surfaces of MPs and MRs (Figure 5). According to previous research, many types of complex blends of ma-

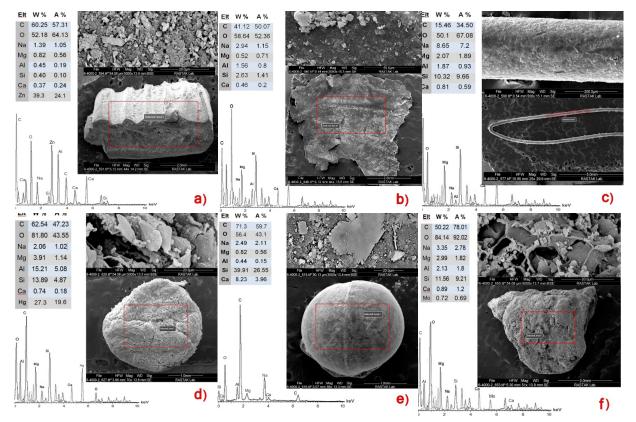


Figure 5. SEM/EDS images and composition of the different MPs and MRs shapes. (A) Fragmented MP; (B) Film MP; (C) Fiber MP; (D) Foam MP; (E) Sphere MP; (F) Fragmented MR.

Abbreviations: Elt: Element; W%: Weight percentage; A%:Atomic percentage

terials are introduced as polymers with unique characteristics. For instance, polymers can be formulated to have antioxidant features. Such qualities can be achieved by adding Al, Ca, Mg, Na and Si to hydrocarbon polymers (e.g. polyethylene, polypropylene, polystyrene). The primary aim of these additives is to slow down the oxidation cycle [8]. Results of elemental analysis revealed that C and O mainly comprise the fragments, films, fibers, foams and spheres of MPs and fragmented particles of MRs. Apart from the additives in polymers, the presence of elements possibly reflects contamination by extraneous solids that contain Al, Ca, Si, Mg and Zn [19].

The energy dispersive X-ray spectroscopy (EDS) showed that MPs mostly exhibit a strong C peak, sometimes accompanied by a smaller O peak (Figure 5). Therefore, fragments, films, fibers, foams and spheres of MPs and fragmented MRs could not be dismissed as non-plastic, as evident from their density and chemical composition. The fragment EDS spectrum revealed a significant carbon peak with suspended quasi-flake particles. Also, it showed additional elements, e.g. Si, Mg, Al, Na, Ca and Zn (Figure 5A). The films, fibers, spheres and foams showed a strong C peak with trace amounts of Si, Mg, Al, Na and Ca (Figure 5B, E) and high amounts of Hg, especially in the foam shape. Also, fragmented MRs exhibited a strong C peak with trace amounts of Si, Mg, Al, Na, Ca and Mo (Figure 5F). These pieces were counted as MPs and MRs because of their strong C signal in EDS.

4. Conclusions

MPs were more abundant in young and medium-aged landfill cells. A lower diversity of polymer types was observed in older landfills. Possible reasons were an enhanced amount of plastic production and usage, distribution of plastic waste by wind and animals, along with the possible fragmentation or degradation of MPs in the landfills and in the MSW Transfer Station. The degree of contamination by MPs and MRs in our study area exceeded those reported by of many comparable landfills and MSW Transfer Stations worldwide. The distribution pattern may reflect the quantity and the composition of plastic waste existing in the municipal solid waste of Ahvaz, which is a function of the life style, economic situation, waste management regulations and industrial structure in the community of this case study. It is expected that these results would have an important impact on waste collecting management and transport systems, landfill management and even on the disposal of plastic waste. To minimize the plastic input into the ecosystem, it is imperative to collect and reuse plastic fragments appropriately and responsibly.

Ethical Considerations

Compliance with ethical guidelines

There were no ethical consideration to be considered in this research.

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Authors' contributions

Conceptualization and supervision: Mahboobeh Cheraghi and Zhaleh Mahdavi Soltani; Methodology: Neematollah Jaafarzadeh; Supervision: Haman Tavakkoli.

Conflict of interest

The authors declare no conflict of interest.

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