Small plastic debris in sediments from the Central Adriatic Sea: types, occurrence and distribution

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Abstract

This is the first survey to investigate the occurrence and extent of microplastic contamination in sediments collected along a coast-open sea 140 km-long transect in the Central Adriatic Sea. Plastic debris extracted from 64 samples of sediments were counted, weighted and identified by Fourier-transform infrared spectroscopy (FT-IR). Several types of plastic particles were observed in 100% of the stations. Plastic particles ranged from 1 to 30 mm in length. The primary shape types by number were filaments (69.3%), followed by fragments (16.4%), and film (14.3%). Microplastics (1-5 mm) accounted for 65.1% of debris, mesoplastics (5-20 mm) made up 30.3% of total amount, while macro debris (>20 mm) accounted for 4.6%. of total plastics collected. Identification through FT-IR spectroscopy evidenced the presence of 6 polymer types: the majority of plastic debris were nylon, polyethylene and ethylene vinyl alcohol copolymer. Our data are a baseline for microplastic research in the Adriatic Sea.

Keywords

Microplastics; Polymer composition; Adriatic Sea; FT-IR spectroscopy

1. Introduction

World production of plastics has strongly expanded, from 1.7 million tonnes in 1950 to 322 million tonnes in 2015 (Plastic Europe, 2016). Discarded "end-of-life" plastic accumulates particularly in marine habitats (Derraik, 2002). Marine plastic litter results from both land and sea-based sources and once at sea, larger items tend to either fragment or sink, and then accumulate on the coastline or on the seafloor, harming wild life and marine food chains (Avio et al., 2017). While pictures of macroplastic debris in ocean gyres (Moore at al. 2001) and of the excessive accumulation of plastics on coastlines worldwide (Galgani et al., 2015) have fostered the awareness of plastic pollution, small plastic debris, defined as microplastics in a size range of <5 mm (Barnes et al., 2009), have emerged as an imminent source of plastic contamination in the marine environment only recently, as a consequence of their eluding presence in sediments and seawater (Andrady 2011). The assessment of marine microplastic pollution is relatively recent, and extensive areas of seas remain yet poorly explored. This is the case of the Mediterranean Sea (UNEP/MAP/MEDPOL, 2009), whose shores house around 10% of the global coastal population, while the basin constitutes one of world´s busiest shipping routes, and receives waters from densely populated river catchments (e.g. Nile, Ebro, Po, Rhone). Contamination by small plastic debris in the Mediterranean is a problem whose extent is only recently been recognized (Gago et al., 2015). In their review, Cózar et al. (2015) reported that floating small plastics abundances in the Mediterranean Sea were similar to those found in the Pacific Ocean gyres, while Woodall et al. (2014) reported of microplastic pollution in sediments from deep cores.

Located in the central Mediterranean, the Adriatic Sea is an elongated basin, with its major axis in the NW-SE direction, between Italy and the Balkans. The northern section is very shallow, with an average depth of about 40 m, while the central one is on average 140 m deep, with the Pomo Depressions reaching 260 m. Along the Italian coast a large number of rivers discharge into the northern and central parts of the basin, being the Po River the most relevant. The Adriatic Sea is characterized by one of the greatest floating plastic particles pollution among Mediterranean regions (Suaria and Alliani, 2014). Liubartseva et al. (2016), estimating the mean particles half-life (i.e., the time after release at which 50% of the particles still remain at the sea surface) in approximately 43.7 days, concluded that the Adriatic Sea is a highly dissipative system with respect to floating plastics (in contrast to the global ocean, where the half-life time of particles equals 19 years), and suggested that the main sink of floating plastics is partitioned between the shoreline and the seafloor, posing additional risk to such ecosystems. Although the distribution and accumulation of small plastic debris in Adriatic shorelines and at the sea surface is relatively documented (Laglbauer et al., 2014; Liubartseva et al., 2016; Munari et al., 2017), contributions to minimize the knowledge gap on benthic small plastic debris are still needed. To date, studies dealing with benthic small plastic debris on the Adriatic seafloor covers only few, very restricted, geographical areas: the Venice lagoon (Vianello et al., 2013), and the Telascica Bay (Blăsković et al., 2017). Larger scale data on benthic macro-litter were recently given by Strafella et al. (2015) and Pasquini et al. (2016), who investigated marine litter abundance and composition in the Adriatic with bottom trawl nets. Larger scale data on benthic small plastics are lacking.

Taking into account the global distribution and implications of small plastic debris and the early stages of studies dealing with microplastics deposition in Mediterranean sediments, and that microplastics is one of the descriptors of the Marine Strategy Framework Directive, MSFD (Gago et al., 2016), with the present study we wanted to assess, for the first time in the Central Adriatic, the quality and quantity of small plastic debris occurring in the seafloor to address the gap in knowledge and to serve as a baseline for future comparisons.

2. Materials and Methods

2.1 Study area and sampling procedures

The survey was conducted in the framework of a monitoring programme (MONITA: HVDC 500 kV cc Italy-Montenegro submarine connection, carried out by Terna SpA), whose main objective was to provide information on benthic invertebrates and environment in the Central Adriatic, however anthropogenic waste data were also gathered. The sampling campaign was carried out with the research vessel "Kiya" in the Central Adriatic Sea, in November 2015. Sediment samples were taken at 16 stations located along a 140 km-long, E-W transect in Italian territorial waters from the town of Pescara to the island of Pianosa, using a Van Veen grab (area 0.1 m^2). Each station was sampled in 4 replicates; at each station, replicates were gathered at a distance of several hundred meters from each other. Sediments were sieved on board on a 1 mm mesh, so the smallest size of gathered debris was 1 mm. In Table 1 the characteristics of the sampled stations are reported.

2.2 Sample analyses

At our laboratories, the plastic debris in sediment samples were removed under a dissection microscope (Nikon SMZ45T, magnification 3.35-300x), counted and weighted to the nearest 0.0001 g. The identified plastics were measured at their largest cross-section using calipers and classified into three groups: micro (1-5 mm), meso (>5–20 mm), and macro (>20 mm) (Gago et al., 2015). There is no general consensus on a specific size nomenclature: Barnes et al. (2009) suggested that microplastics be defined as <5 mm particles and this approach has been used in our study. Plastic debris were also categorized according to shape, i.e. filament, film, and fragment. Filaments are cylindrical, pigmented and transparent; films tend to be flat, hard and do not tend to break or deform when pressed with a dissecting needle; fragments are particles of different colors that are hard or flexible but do not tear when pulled, nor do they shatter into many small pieces when pressed with a dissecting needle.

Plastic debris composition at the 16 stations was investigated by means of ordination analysis (nMDS) based on the Bray-Curtis similarity index calculated on quantity data.

Fourier-transform infrared spectroscopy (FT-IR) analysis of plastic debris was carried out with a CARY 600 FT-IR (Agilent Technologies) instrument. Measurements were carried out in attenuated total reflectance (ATR) configuration, with a Pike Miracle diamond cell. Tests were carried out at 25°C in dry air. Particles were identified by comparing FT-IR absorbance spectra of the microplastics to those in a polymer reference library.

3. Results

In Table 1, sedimentary composition at 16 stations is shown. Seafloor was characterized by particles ranging from gravels (diameter between 4-2 mm) to clay (diameter <0.0039 mm), according to the Wentworth grain-size classification. The fraction of finer sediments (silt + clay) was dominant from St.4 onwards, making up over 80% at the majority of stations.

A total of 64 sediment samples were analyzed from the 16 stations. Some examples of plastic debris collected during the study are shown in Fig. 1. Not all sediment samples contained plastics, but several types of plastic particles were observed in all the 16 stations. Plastic particles in the samples ranged from 1 to 30 mm in length. The samples contained both filaments, film and fragments in a range of colors (mostly red, orange, green and blue), implying that particles may have originated from multiple sources.

The greatest plastic abundance by number (Fig. 2) was observed at St.11 (87.5 ± 93.6 debris m^{-2}), while by weight at St.14 (1.7 ± 3.2 g m^{-2}); the lowest mean values by number and by weight was at St.8 (2.5 ± 5.0 debris m^{-2}, and 0.002 ± 0.004 g m^{-2} respectively). Between stations near the coast (St.1-5) and distant (St.10-16), there are stations where the plastic concentration was lower. The primary shape types by number were filaments (69.3%), followed by fragments (16.4%), and film (14.3%). In Table 2 the average abundance of shape type of plastics collected is shown, together with the average abundance of plastics according to size. In terms of numerical abundance, microplastics accounted for 65.1% of the total amount found, mesoplastics made up 30.3% of total amount, while macro debris accounted for 4.6%.

Ordination analyses through nMDS showed a clear pattern in concentration of shape types (Fig. 3) and size (not shown for brevity) of plastics, with a group of stations segregated together as they have higher concentrations, and other stations apart due to their lower amount of debris.

Identification through FT-IR spectroscopy evidenced the presence of 6 polymer types: polyethylene (PE), polypropylene (PP), Nylon 6.6 (Nylon), linear low-density polyethylene-octene copolymer

(LLDP/Oct), ethylene vinyl alcohol copolymer (EVOH), and thermoplastic polyurethane (TPU). The composition by abundance of polymer type is shown in Fig. 4a, and by weight in Fig. 4b. Considering abundance, the majority of plastic debris were Nylon (46.7%), PE (28.1%), and EVOH (14%), followed by PP (4.6%), TPU (3.9%), and LLDP/Oct (2.7%). By weight, PE (52.9%) was the most represented polymer type, followed by EVOH (17.7%), Nylon (12%), PP (8.7%), LLDP/Oct (8.3%), and TPU (0.4%).

4. Discussion

We gathered seafloor small plastic debris (>1 mm) as a by-catch while sampling benthic macroinvertebrates along a 140 km-long transect, from the coast to the open sea. Because of the high cost involved with sampling the seafloor in the open sea, no historical data are available from Italian seafloors for assessing trends in microplastics, neither specific monitoring programs have been developed up to date. Despite some limitations, such as the minimum size of plastics collected, this "by-catch study" is the first study to present an assessment of microplastics pollution in the Central Adriatic Sea. "By-catch studies" like this one may help to address the gap in knowledge and to make available otherwise unavailable data for future comparisons for instance in the framework of the MSFD implementation (e.g. Ramirez-Llodra et al., 2013).

We found small plastics particles in 69% of the sediments (44 out of 64) collected in the Central Adriatic Sea. The collected plastics were categorized in 3 principal categories: filaments (69.3%), fragments (16.4%), and film (14.3%). In the Telascica Bay (Eastern Adriatic), Blăsković et al. (2017) found that filaments represented 90% of all seafloor plastics. The main source of our debris was attributed to the breaking down of larger items. Fragmentation of larger items is mainly driven by photo-oxidative, thermal- and biodegradation (Andrady, 2011). Microplastics comprised the majority of the plastic debris (65.1%), with a declining plastic size with increasing plastic debris abundance. Barnes et al. (2009) reported a generalized decrease in the mean size of plastic debris in the global environment, along with the increasing abundance of such particles due to continuous degradation.

All plastics in our samples were secondary products derived from degradation and fragmentation of larger fragments, but it was not possible to attribute a specific source or a specific activity of origin if not for some fishing lines filaments. Contrary to other studies which report high microplastics concentrations in sediments close to densely populated areas (e.g. Van Cauwenberghe et al., 2015), high quantities of small plastics were found in the open sea floor, far-away from densely populated areas. Recent literature addressed the apparent paradox of the missing fraction of microplastics in coastal waters and their pre-eminent fate in the deep sea (Woodall et al., 2014). Densities hotspots of plastics found at stations farthest from the coast (stations 10 to 16: 68.9% of all plastics found in this study) could be originated from marine-based sources including fishing vessels, merchant vessels and recreational boats. Indeed, this part of Central Adriatic is a busy shipping route with thousands ships passing by per year (https://www.marinetraffic.com). This result supports other works suggesting that areas along shipping traffic have high presence of microplastics (e.g. Claessens et al., 2011). Conversely, we suspect that plastics found in shallower sites (station 1 to 6: 28.2% of all plastics found in this study) originate from the densely populated coastline (with the towns of Pescara, Francavilla, Ortona, and the estuary of the Aterno-Pescara River) and consequent high anthropogenic pressures. Spatial distribution of plastics (Fig. 2) grossly shows two peaks of density, one near the coast (stations 1-5) and one far from the coast (stations 10-16), with intermediate sites (such as stations 6-9) where the presence of plastics is very scarce. In the Central Adriatic Sea, a vertical thermohaline front, running parallel to the coast and extending throughout the water mass, separates the coastal waters from the open sea ones (Artegiani et al., 1997): this might retain the materials that flow from rivers and other water sources within the coastal area. Assessing seafloor macrolitter in the Adriatic, Strafella et al. (2015) found the highest concentration of litter in the stations close to the coast within 30 m depth, while the lowest amount was recorded offshore between 50 and 100 m.

Our study provides insights into the polymer types found as small debris in Adriatic sediments, from which their sources may be inferred. Through FT-IR spectroscopy we evidenced the presence of 6 plastic types. The density of plastics can vary considerably depending upon the type of polymer and the manufacturing process. For instance, the density of PE ranges from 0.92 to 0.96 g cm^{-3}, LLDP/Oct from 0.91 to 0.94 g cm^{-3}, PP from 0.90 to 1.00 g cm^{-3}. These microplastics can be carried long distances because they are less dense than seawater (~1.025 g cm^{-3}). Other plastics are denser than seawater (e.g. Nylon from 1.13 to 1.15 g cm^{-3}, EVOH from 1.12 to 1.22 g cm^{-3},TPU from 1.14 to 1.20 g cm^{-3}), and tend to settle on the sea bottom. The plastic polymers found in this study are used in a wide range of domestic and industrial applications, including packaging, textiles and electronics, which indicates diverse sources. However, the precise origin of individual microplastic debris cannot currently be established. Of all the plastic debris collected in this study, 64.5% by numbers (30% by weight) of microplastics were made of EVOH, Nylon and TPU, all polymers denser than seawater. These dense microplastics are unlikely to have drifted independently in the upper sea. EVOH is commonly used as an oxygen barrier in food packaging. Nylon, which forms the largest proportion of plastic filaments in this study, is a common polymer detected in some other microplastics studies (Claessen et al., 2011): it is used for making ropes and fishing lines, draperies, parachutes, etc. TPU is used for sporting goods, medical devices, inflatable rafts, and a variety of extruded film, sheet and other applications (e.g. outer cases for mobile phones). Of the remaining plastic debris 35.5% by numbers (and 70% by weight) were made of PE, LLDP/Oct, and PP, which are principally used to make packaging that is used once and then discarded. Our findings agree with previous studies of plastic debris in which packaging for food were among the most abundant types of debris found in marine habitats.

Data presented in this study provide baseline information of the distribution and types of seafloor small plastics in the Adriatic Sea, contributing to the efforts of the MSDF. Studies like this are crucial for undertaking policy reforms and to assess the economic impact of marine microplastic pollution.

5. Conclusions

This study gives a first insight into microplastic pollution in the Central Adriatic seafloor. It provides information on concentration and spatial distribution of plastic particles in the Pescara-Pianosa area, and this data could be used as reference or baseline data to test the effectiveness of any reduction measures adopted to address the MSFD requirements. Moreover, the recent MSFD has highlighted the existing gaps in the knowledge of spatial patterns and typology of plastic debris in European Seas. Our understanding on the amount and distribution of microplastics in the Mediterranean seafloor is extremely limited, due to the high cost involved with sampling in the open sea. This study also supplements the role of routine benthic surveys performed by national authorities (e.g. Italian ARPA) and could be a useful tool for the assessment of microplastics in the marine environment, at no additional cost.

Acknowledgements

We are very grateful to Mr. Patrizio Fontana and Mr. Albino Moretti for their help with the sampling. Our sincere gratitude to all crew members of the vessel "Kiya" for their support at sea. We acknowledge an anonymous reviewer for constructive criticism.

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Figures

Fig. 1. Examples of the collected plastic debris.

Fig. 2. Abundance and standard deviation of plastic debris at the 16 stations.

Fig. 3. Ordination plots through nMDS of shape types data of plastic debris.

Fig. 4. Composition of plastic debris collected at the 16 sampling sites according to (a) type of polymer, and (b) weight (thermoplastic polyurethane: TPU, polyethylene: PE, polypropylene: PP, linear low-density polyethylene/octene copolymer: LLDPE/Oct, Nylon 6.6: NYL, ethylene vynil alcohol copolymer: EVOH).

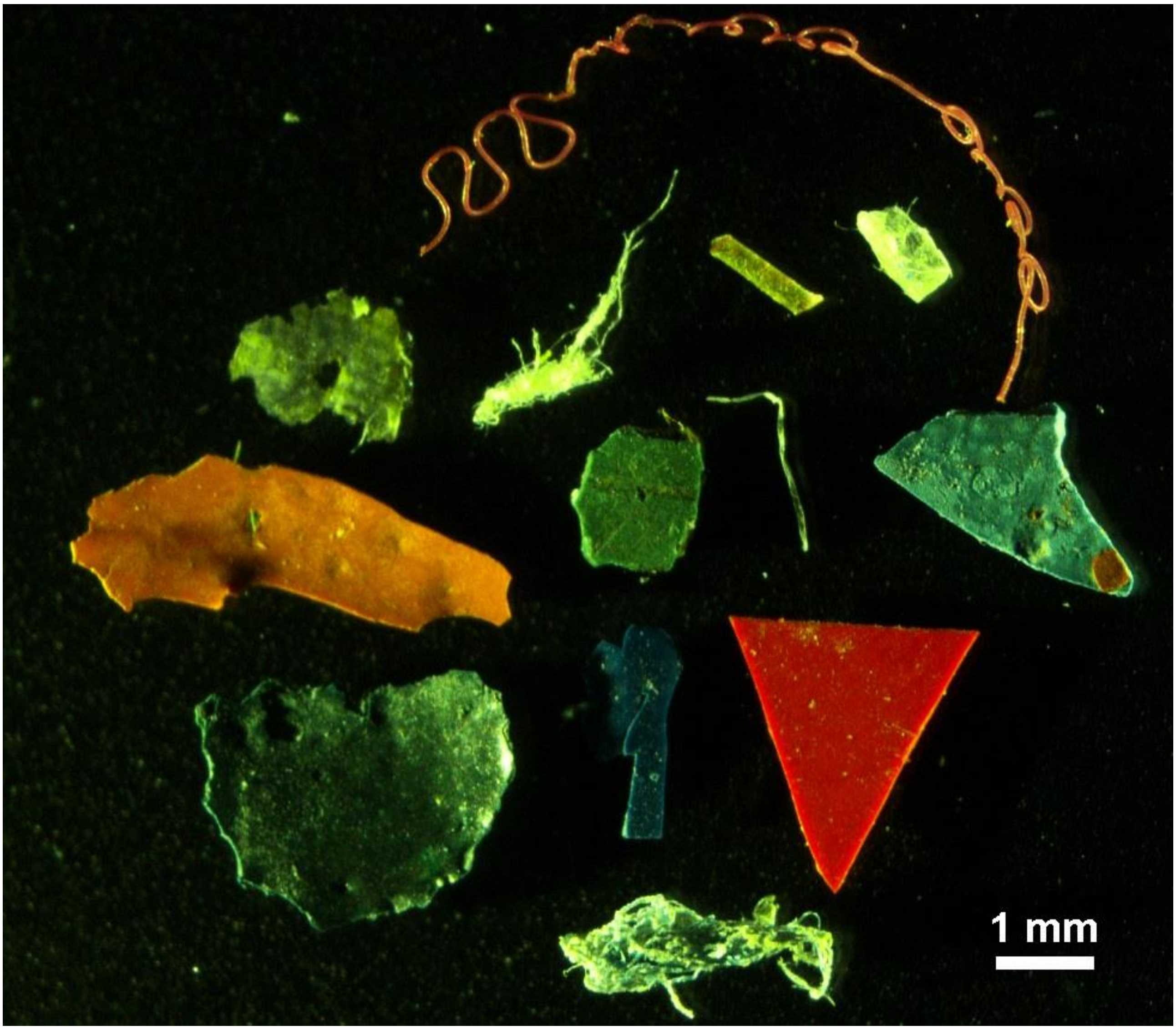

Fig. 1

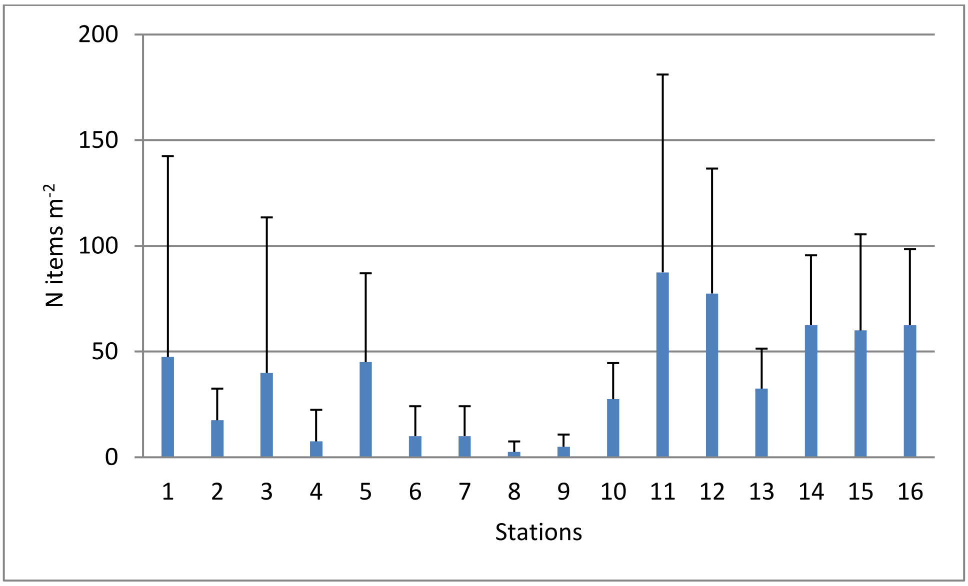
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Fig. 2

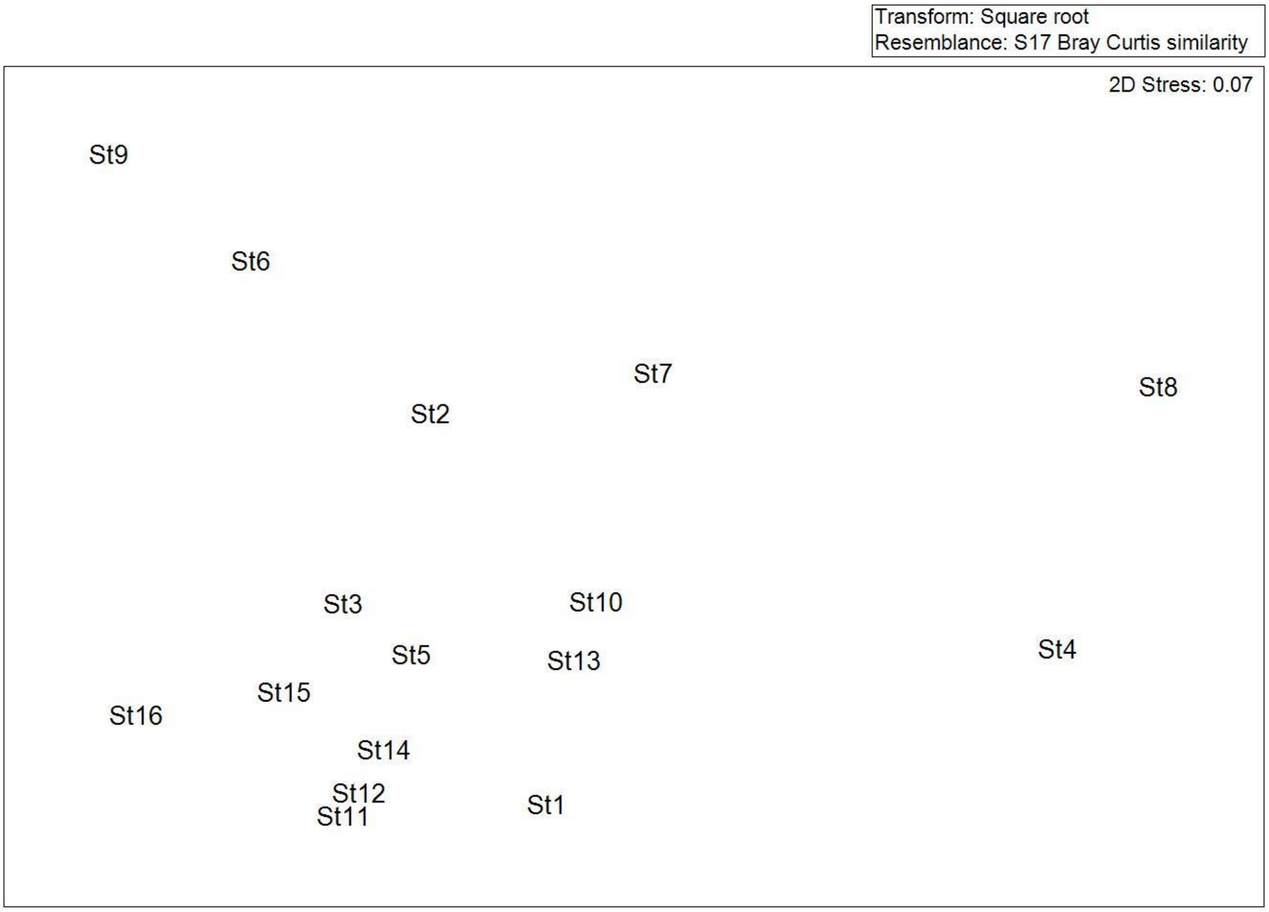
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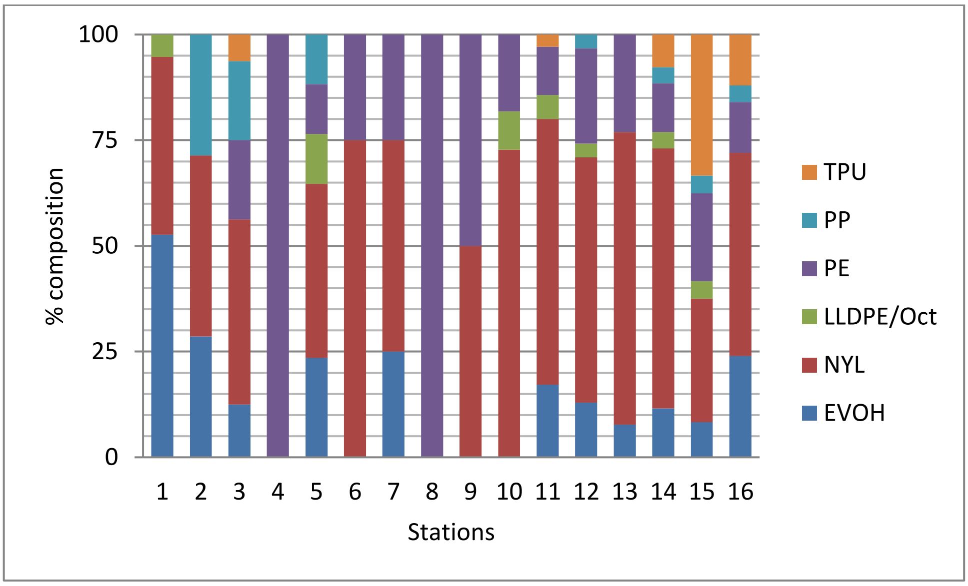
Fig. 3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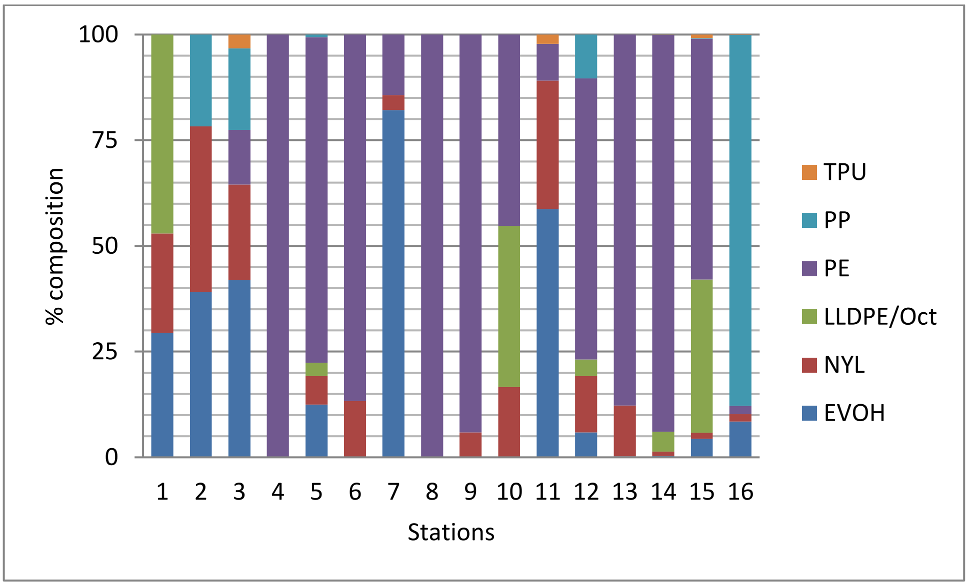
NYL
EVOH

a)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1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
Stations
TPU
PP
PE
LLDPE/Oct
NYL
EVOH

b)

Fig. 4

Table 1.
Characteristics of the sampled stations.

Station	Lat WGS84 *DDMMSS.dd*	Long WGS84 *DDMMSS.dd*	Depth *m*	Gravels *%*	Sand *%*	Silt *%*	Clay *%*
1	422722.135	141525.361	7	<0.1	70.3	24.2	5.5
2	422749.211	141617.727	12	0.2	44.9	26.7	28.2
3	422818.279	141713.970	16	0.5	46.8	34.7	18.0
4	422841.728	141759.365	19	0.8	16.8	46.9	35.5
5	422906.371	141919.475	23	0.5	24.8	47.7	27.0
6	422911.468	142009.131	27	< 0.1	17.7	56.6	25.7
7	422902.623	142237.978	47	< 0.1	1.4	66.8	31.8
8	422845.206	142613.719	70	1.3	2.1	53.8	42.8
9	422827.571	142950.706	83	< 0.1	2.1	36.2	61.7
10	422809.807	143327.853	92	< 0.1	0.6	40.4	59.0
11	422751.858	143705.802	100	< 0.1	1.0	39.3	59.7
12	422223.749	153520.037	142	< 0.1	2.6	24.2	73.2
13	422155.845	153855.384	138	< 0.1	2.0	38.8	59.2
14	422127.828	154230.678	132	< 0.1	6.0	25.7	68.3
15	422058.645	154605.681	130	0.2	7.8	34.0	58.0
16	421907.522	154921.843	119	0.8	15.8	32.8	50.6

Table 2.
Shape type and size of plastics collected. Values represent average abundance (pcs *per* square meter) and standard deviation.

Station	Filament	Film	Fragment	Micro *(1-5 mm)*	Meso *(5-20 mm)*	Macro *(>20 mm)*
1	45 ± 90	0	2.5 ± 5	45 ± 90	2.5 ± 5	0
2	12.5 ± 15	2.5 ± 5	2.5 ± 5	75 ± 15	7.5 ± 9.6	2.5 ± 5
3	17.5 ± 28.7	15 ± 30	7.5 ± 15	27.5 ± 48.6	12.5 ± 25	0
4	0	0	7.5 ± 15	7.5 ± 15	0	0
5	32.5 ± 37.7	5 ± 5.8	7.5 ± 5	27.5 ± 26.3	15 ± 12.9	2.5 ± 5
6	7.5 ± 9.6	2.5 ± 5	0	2.5 ± 5	0	7.5 ± 9.6
7	7.5 ± 9.6	0	2.5 ± 5	7.5 ± 1.5	0	2.5 ± 5
8	0	0	2.5 ± 5	2.5 ± 5	0	0
9	2.5 ± 5	2.5 ± 5	0	0	2.5 ± 5	2.5 ± 5
10	20 ± 18.3	0	7.5 ± 5	12.5 ± 5	15 ± 12.9	0
11	72.5 ± 83.4	7.5 ± 15	7.5 ± 15	57.5 ± 70.4	27.5 ± 25	2.5 ± 5
12	52.5 ± 29.7	5 ± 10	17.5 ± 17	55 ± 52.6	22.5 ± 9.6	0
13	25 ± 12.9	0	7.5 ± 9.6	20 ± 8.2	12.5 ± 12.6	0
14	50 ± 21.6	5 ± 10	10 ± 10.2	42.5 ± 22.2	15 ± 12.9	5 ± 5.8
15	22.5 ± 28.7	22.5 ± 32	15 ± 13	35 ± 25.2	25 ± 23.8	0
16	45 ± 23.8	17.5 ± 22.2	0	37.5 ± 27.5	22.5 ± 5	2.5 ± 5