Environmental Pollution xxx (xxxx) xxx

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

# Quantitative and qualitative evaluation of plastic particles in surface waters of the Western Black Sea☆

Iulian Pojar [a], Christian Kochleus [b], Georg Dierkes [b], Sonja M. Ehlers [b], Georg Reifferscheid [b], Friederike Stock [b,*]

[a] National Institute of Research and Development for Marine Geology and Geo-ecology - GeoEcoMar, 23-25 Dimitrie Onciu, 024053, Bucharest, Romania
[b] German Federal Institute of Hydrology, Am Mainzer Tor 1, 56068, Koblenz, Germany

ARTICLE INFO

*Article history:*
Received 18 April 2020
Received in revised form
21 September 2020
Accepted 23 September 2020
Available online xxx

*Keywords:*
Black Sea
Danube Delta
Plastic pollution
Spectroscopy
Romanian coast

ABSTRACT

Microplastic abundances have been studied intensively in the last years in marine and freshwater environments worldwide. Though several articles have been published about the Mediterranean Sea, only few studies about the Black Sea exist. The Black Sea drains into the Mediterranean Sea and may therefore significantly contribute to the Mediterranean marine pollution. So far, only very few articles have been published about micro-, meso- and macroplastic abundances in the Western Black Sea. In order to fill this knowledge gap and to decipher the number of plastics on the water surface, 12 samples were collected from surface waters with a neustonic net (mesh size 200 μm) in the Black Sea close to the Danube Delta and the Romanian shore. Organic matter was digested and plastic particles were isolated by density separation. The results of visual inspection, pyrolysis GC-MS (for microplastics) and ATR-FTIR (for mesoplastics >5 mm) revealed an average concentration of 7 plastic particles/m$^3$, dominated by fibers (~76%), followed by foils (~13%) and fragments (~11%). Only very few spherules were detected. The polymers polypropylene (PP) and polyethylene (PE) dominated which is in line with other studies analyzing surface waters from rivers in Western Europe as well as in China. Statistical analyses show that the plastic concentration close to the mouth of the Danube River was significantly higher than at four nearshore regions along the Romanian and Bulgarian coastline. This could be explained by plastic inputs from the Danube River into the western part of the Black Sea.



## 1. Introduction

In the last two decades the scientific community has intensively investigated plastic particles in different aquatic and terrestrial environments (Crawford and Quinn, 2017; Wagner and Lambert, 2018). Plastic research has become interdisciplinary with various papers published on marine and freshwater environments including water and sediment (Blettler et al., 2018; Mani et al., 2019; Peng et al., 2018; Schwarz et al., 2019), organisms (Besseling et al., 2018; Ehlers et al., 2019; Triebskorn et al., 2019), soils (de Souza Machado et al., 2018; He et al., 2018) or methodological approaches (Mai et al., 2018; Prata et al., 2019; Stock et al., 2019).

Being located between South-East Europe and Asia Minor, the Black Sea is an important basin for aspects such as ecology, geology, tourism, economic or international affairs. The Black Sea has a catchment basin of 2 million km$^2$ draining 21 countries (Lehmann et al., 2015) with a total population of ca. 180 million (Lehmann et al., 2015). It is a narrow semi-enclosed basin characterized by a high deposition of multiple pollution forms (Bakan and Büyükgüngör, 2000; Topçu et al., 2013; Tuncer et al., 1998) and is often described as a highly degraded ecosystem (BSC, 2007) due to several geomorphologic and socio-economic factors: intense maritime navigation, high discharge of polluted freshwater from several large rivers (Danube, Dnieper, Bug, Dniester, Don, Kuban, Rioni), numerous industrialized harbors and cities surrounding the sea, intense fishing activities (FAO, 2015), strong tourism, etc. Heavy metal pollution (Duliu et al., 2009; Sarı et al., 2018), organochlorine pesticides (Ozkoc et al., 2007) and water and sediment quality (Akbal et al., 2011) have been studied intensively; however, only few studies about micro- (<5 mm), meso- (5–25 mm) and macroplastic pollution (>25 mm; GESAMP, 2019) in the Western Black

☆ This paper has been recommended for acceptance by Eddy Y. Zeng.

* Corresponding author.
*E-mail address:* stock@bafg.de (F. Stock).

https://doi.org/10.1016/j.envpol.2020.115724
0269-7491/

Please cite this article as: I. Pojar, C. Kochleus, G. Dierkes *et al.*, Quantitative and qualitative evaluation of plastic particles in surface waters of the Western Black Sea, Environmental Pollution, https://doi.org/10.1016/j.envpol.2020.115724

Sea have been published. Topçu et al. (2013) studied marine litter, Suaria et al. (2015) the pollution of sandy beaches and surface waters of the Southwestern Black Sea, Moncheva et al. (2016) marine litter in the bottom sediments of the Western Black Sea and Simeonova and Chuturkova (2019) the abundance of marine litter along the Bulgarian Black Sea coast. Popa et al. (2014) investigated microfibers in marine habitats and Aytan et al. (2016) examined microplastic particle concentrations in surface waters along the Southwestern coast of the Black Sea. Furthermore, Öztekin and Bat (2017) analyzed microplastics in the water column and surface waters of the Southern Black Sea and Aytan et al. (2018) the abundance of microplastic particles in copepods (southwestern part). Microplastics in beach sediments were studied for the first time by Popa et al. (2014) at five sites of the Romanian Black Sea coast.

To add to the current understanding of plastic pollution in the Black Sea, this study has the goal to evaluate plastic concentrations at several locations of the Western Black Sea. Considerable quantities of plastics (4.2 t/day, Lechner et al., 2014) together with sediment and water are transported via the Danube River, especially during the flood season. It is assumed that the north-south surface currents (Shapiro, 2019) strongly contribute to a distribution of these particles not only nearby the southern area of the Danube Delta, but also further south, along the Romanian and the Bulgarian coast. Berov and Klayn (2020) describe similar plastic particle loads as the ones reported in the present study.

## 2. Methods

### 2.1. Study area

The Western Black Sea from the Danube Delta south to the Bulgarian border was selected for a comprehensive evaluation of surface water in the Black Sea. The study represents an initiative for evaluating the plastic particles in the surface waters of the Western Black Sea, with respect to both studies in the Southern Black Sea area (Aytan et al., 2016, 2018) and Guidelines for the monitoring and assessment of plastic litter and microplastics in the ocean (GESAMP, 2019). Possible sources of plastics were taken into account such as the mouth of the Danube Delta (branches Sulina and Sf. Gheorghe) which discharges ca. 6500 $m^3$ freshwater per second into the Black Sea (Stancik et al., 1988) as well as main harbors and cities (Constanta and Mangalia) (Fig. 1). For investigating the pollution degree, sampling areas with a high ecological importance (e.g. biosphere reserves) were also targeted: the Danube Delta coast (proximal waters) and areas located nearby tourism resorts predominantly situated between the cities of Constanta and Mangalia.

### 2.2. Sampling

Samples were collected during one campaign in August 2018 organized by NIRD GeoEcoMar by using the research vessel RV Mare Nigrum (see supplement S1 for coordinates). Sampling areas were chosen on the one hand as being close to possible sources of plastics and to tourism resorts and on the other hand close to natural areas (Luo et al., 2019; Siegfried et al., 2017) (Fig. 1). Six samples were taken near the Romanian coast 2–5 km from the shore, four samples 10–30 km and two other samples 46 km and 115 km east of the shore (Fig. 1). The floating plastic particles were sampled with an attached neustonic net (HydroBios, mouth opening: 70 × 40 cm, length of net bag: 260 cm) that was hooked onto a side crane. The net mesh size (200 μm) is comparable to the study by Aytan et al. (2016) who collected samples from the top water layer (25–30 cm). The surface water (upper 20 cm) was sampled for 5 min over a distance of about 300 ± 100 m at a speed of about 1.7 knots. The filtered water was calculated with a manual flowmeter fixed to the opening of the net (see Scherer et al., 2020). The water samples were transferred into pre-cleaned glass jars, using distilled water for rinsing, and then frozen at −20 °C. Between each sampling, nets were cleaned with distilled water to prevent any contamination from the vessel.

### 2.3. Sample preparation

The preparation process was performed at the German Federal Institute of Hydrology. The samples were transferred into individual pre-cleaned glass beakers and organic matter was digested using a reagent composed of 10 M potassium hydroxide solution (KOH) and hydrogen peroxide ($H_2O_2$, 30%) (1:1; 30–50 mL per sample; see Ehlers et al., 2019; Scherer et al., 2020). After being agitated for 5–7 days, samples were neutralized with formic acid (3.89 mL per 10 mL KOH). During the agitation, the glass jars were covered with parafilm to prevent airborne microplastic contamination. Microplastic particles were isolated in a separation funnel with potassium formate ($CHKO_2$) solution (3.6 g/mL of the sample) for reaching a final density of 1.6 g/mL. This is an appropriate density as most plastics have a lower density and will therefore float in that solution. After 3–4 days, pressure filtration (Sartorius Stedim, Göttingen, Germany) was conducted on glass fiber filters (GE Healthcare Life Sciences, Whatman, GF/D Cat. No. 1823-047, diameter: 47 mm, pore size: 2.7 μm). The filters were stored in individual aluminum bowls and covered for protection.

### 2.4. Identification of micro- and mesoplastic particles

Micro- and mesoplastic particles were identified by means of optical (visual identification), spectroscopical (FTIR) and spectrometrical analysis (pyrolysis GC-MS). ATR-FTIR was chosen for all mesoplastics and pyrolysis GC-MS for selected microplastic particles.

### 2.5. Visual identification

Optical analysis for identifying plastic particles was performed with a digital microscope (Keyence VHX-2000, Osaka, Japan) equipped with 50 and 200 x magnifying lenses. In order to identify particles, color and shape of particles were analyzed (see criteria by Norén, 2007). For identification of microplastics, all particles with a size of 200 μm to 5 mm were taken into account, with the upper limit after Arthur et al. (2009). Additionally, we quantified particles bigger than 5 mm that were identified in low amounts, framing them in the mesoplastic category (5–25 mm; GESAMP, 2019). Particle abundance was based on filtered water and the amount of identified plastic particles (in particles/$m^3$).

### 2.6. Pyrolysis GC-MS

Isolated single particles or fibers were identified by pyrolysis GC-MS using the system described previously (Dierkes et al., 2019). A single particle was pyrolyzed at 600 °C using a split ratio of 1:20 for fibers and 1:50 for particles. For detection, an Agilent MSD 5977B (Santa Clara, CA, USA) in scan mode (40–800 Da) was used. Identification was performed by comparison of the resulting pyrograms with those from the library F-Search 3.4 (Frontier Laboratories, Saikon, Japan; Tsuge et al., 2011) containing >1000 polymers.

### 2.7. Fourier-transform infrared spectroscopy (FTIR)

All mesoplastics with a size >5 mm were measured using the

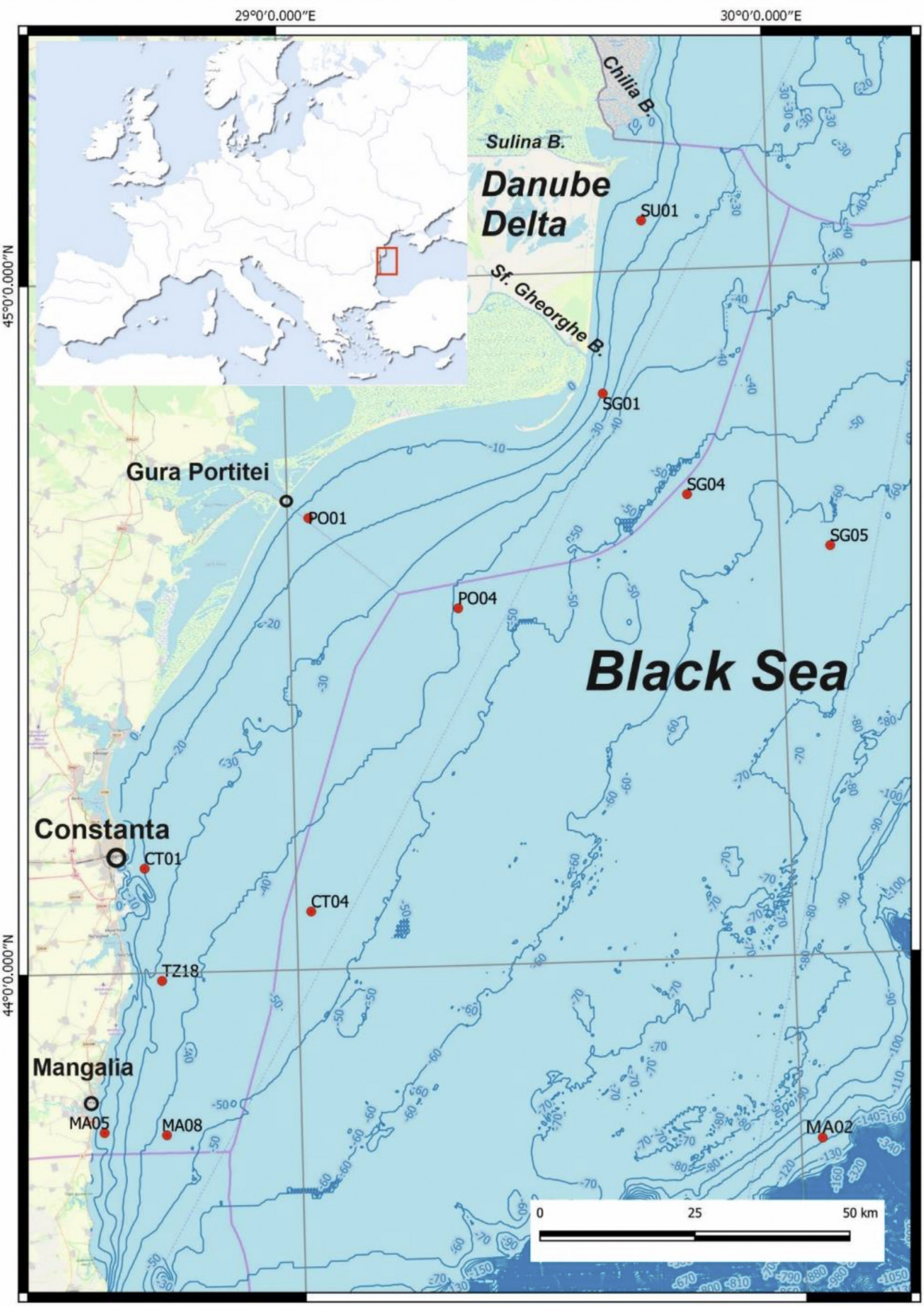


**Fig. 1.** Sampling sites for plastic analyses in the Western Black Sea surface waters.

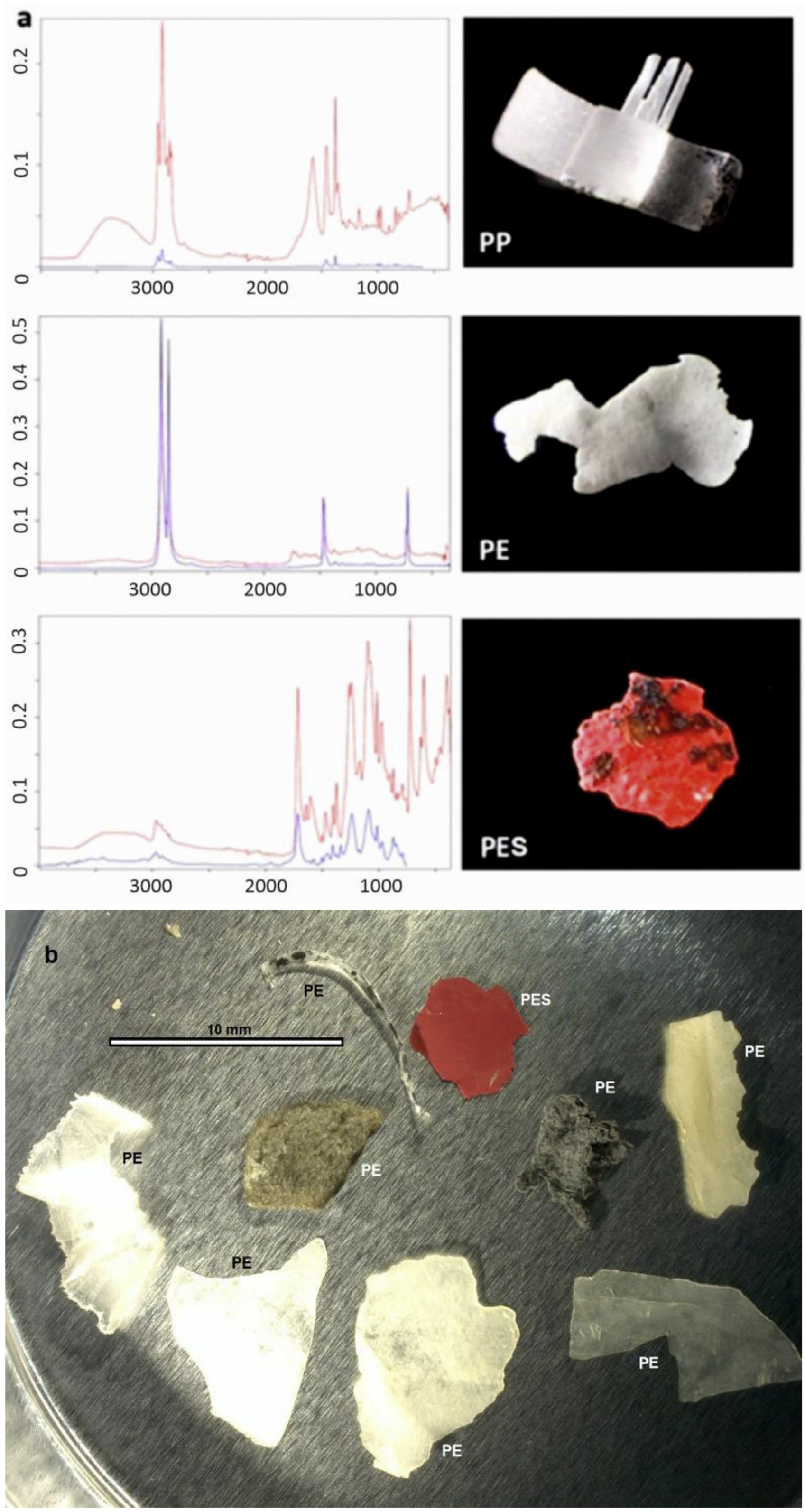


**Fig. 2.** a) FTIR spectra of analyzed mesoplastics (polypropylene (PP), polyethylene (PE), and a particle belonging to the polyester family; PES) measured in ATR mode (red spectra). The blue spectra are reference spectra from the Bruker spectral database; the *x* axis represents the Wavenumber (cm$^{-1}$) and on the *y* axis one can see the absorbance units. b) Photo of selected particles. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

platinum ATR unit (equipped with a diamond) of the Fourier-transform infrared spectrometer (FTIR; Vertex 70, Bruker, Ettlingen, Germany). Analyzing plastic polymer types with methods such as Fourier-transform infrared spectroscopy (FTIR) is essential as up to 70% of particles may be misidentified as plastics during visual analysis (Hidalgo-Ruz et al., 2012). Therefore, in our study representative red, gray, black, white and transparent (colorless) particles were analyzed using an FTIR. The FTIR measurements were performed in attenuated total reflectance mode (ATR) in a wavenumber range of 4000–370 $cm^{-1}$ with 8 co-added scans and a spectral resolution of 4 $cm^{-1}$. The obtained spectra were compared with the Bruker spectral database using the software OPUS 7.5 (Bruker). Only those particles which had a spectrum with a hit quality above 700 were considered as plastics (i.e. Bergmann et al., 2017).

### 2.8. Quality assurance

In order to prevent sample contamination from e.g. dust, the working space was cleaned with ethanol each time before work started. Glass and stainless-steel materials were used for the laboratory work. Moreover, cotton lab coats were worn. During sample preparation, two laboratory blanks were conducted, using same amounts of potassium hydroxide, hydrogen peroxide, potassium formate, formic acid and ultrapure water, which was digested the same way as the other samples and filtered. Correction was applied to each filter. Also, all samples were covered with aluminum foil/parafilm throughout the chemical digestion and storage.

### 2.9. Statistics

Plastic concentrations were analyzed with the Statistica 10 software. Tentative plastic concentrations (with the exception of the unreplicated locations CT04 and MA02) were examined using a balanced ANOVA that compared the mean plastic concentrations between the Danube Delta and the nearshore locations (two locations paired: Danube Delta: SU01 & SG01, nearshore 1: SG04 & SG05, nearshore 2: PO01 & PO04, nearshore 3: CT01 & TZ18, nearshore 4: MA05 & MA08). For the confirmation of all ANOVA assumptions (i.e. variance homogeneity, normality), Cochran C and Shapiro-Wilk-test were used. Moreover, we ran the Tukey Honestly Significant Differences (HSD) test to check which regions differ in plastic load.

## 3. Results

### 3.1. Numerical abundances of plastics in the Western Black Sea

All potential microplastic particles on the filters were visually examined from 200 μm to 5 mm. In total, 3289 particles were counted including 22 particles >5 mm. In all 12 samples, plastic particles were detected (see supplement S2). The results reveal an average concentration of 7 plastic particles per $m^3$. Concentrations ranged from 1.3 particles/$m^3$ (PO04) to 18.6 particles/$m^3$ (SU01) (Figs. 3 and 6). The most dominant form were fibers followed by foils and fragments. Only few fiber clumps and spherules were found in the samples. Of those, 74.6% were identified as fibers, 1.5% as fiber clumps, 12.7% as foils, 11.1% as fragments and 0.1% as spherules (Fig. 4).

Along the western coast of the Black Sea, plastic concentrations in the surface waters were the highest close to the Danube Delta (Fig. 6, SU01: 18.6, SG01: 16.1 particles/$m^3$). The two samples further southeast are characterized by an evenly low amount (SG04: 5.1 particles/$m^3$, SG05: 5 particles/$m^3$) and were similar when compared to the other nearshore regions (PO01 and PO04, CT01 and TZ18, MA05 and MA08). Along the coast to the south close to Gura Portitei, 3.3 particles/$m^3$ were counted (PO01). Several kilometers to the east, the concentration decreased to 1.3 particles/$m^3$ (PO04).

Close to Constanta, the amounts varied (6.2 particles/$m^3$ (CT01) and 2.7 particles/$m^3$ (TZ18)). Close to Mangalia, more plastic particles occurred (7.3 particles/$m^3$ (MA05) and 10.3 particles/$m^3$ (MA08)) while the concentration decreased further to the east (1.2 particles/$m^3$ (CT04) and 9.9 particles/$m^3$ (MA02)).

For all 12 samples, the most dominant particle color was black including 46.6% of all particles (micro- and mesoplastic; see supplement S3). Other colors were white (24.6%), blue (16%), green (6%), red (4%) and yellow (3%).

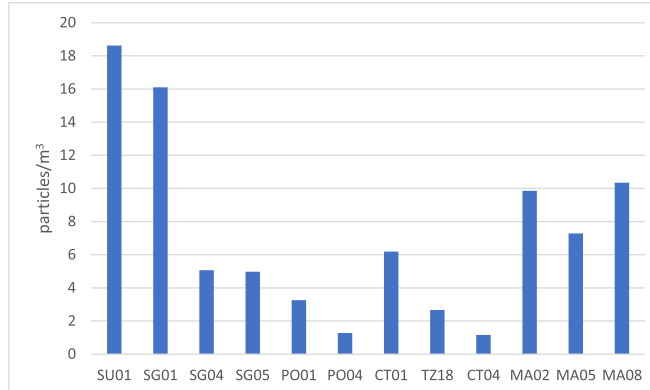


**Fig. 3.** Results of the plastic abundance in the surface waters of the Black Sea.

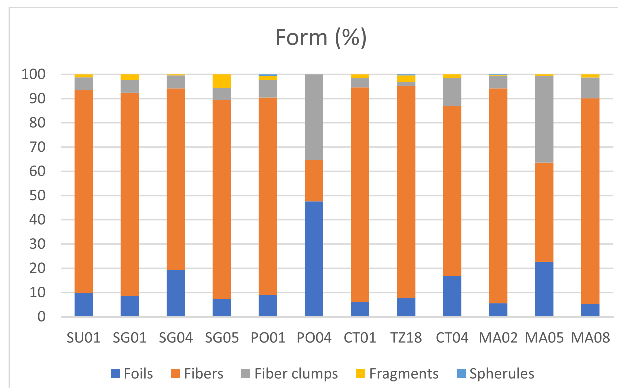


**Fig. 4.** Form of plastic particles (%) identified in the samples.

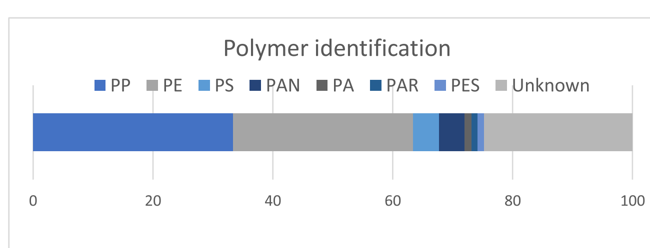


**Fig. 5.** Composition of polymer types (in %) determined by ATR-FTIR and pyrolysis GC-MS analysis in the water samples from the Black Sea.

### *3.2. Contamination control*

Contamination during laboratory analysis was detected on the two blank samples (one for a set of six samples) with an average of 53 ± 20 fibers (>200 μm) per filter. The particles counted on the blank filters were subtracted from each corresponding sample analyzed, taking into account color and morphology of particles.

### *3.3. Statistical analysis*

Five regions were differentiated in the ANOVA. The two samples CT04 and MA02 further to the east of Constanta and 115 km to the east have not been integrated in the statistical analysis as they were not replicated. The ANOVA revealed that there was a significant difference between the five analyzed regions ($F(4,5) = 22.05$, $p = 0.002$) and the Tukey HSD test showed that plastic levels close to the Danube Delta were significantly higher than at the four nearshore locations ($p < 0.05$). However, the nearshore locations did not differ in plastic levels ($p > 0.05$).

### *3.4. Characterization of polymer types*

In total, 93 particles out of 3289 (2.83%) particles were analyzed by means of ATR-FTIR (22 particles) and pyrolysis GC-MS (71 particles). 75% of all particles could be identified as polymers (Fig. 5).

All particles (22) with a size >5 mm were measured with the ATR-FTIR. The analyzed plastics were mainly made of PE (20 particles), but we also found PP (one particle) and one red particle belonging to the polyester family (PES; Fig. 2).

71 particles were measured with the pyrolysis GC-MS. For a representative analysis, the most common forms and different colors were chosen for analysis. The most abundant polymer was polypropylene (PP, 30 particles), followed by polyethylene (PE, 8 particles), polystyrene (PS, 4 particles), polyacrylonitrile (PAN, 4 particles) and polyamide (PA), polyacrylate (PAR) and polyester (PES) (one particle each). 22 particles could not be identified (Fig. 5). Thus, ca. 70% of all particles measured with the pyrolysis GC-MS could be verified as polymers. The fibers made up ~46% of all identified particles. 75.8% of the identified fibers were made of PP (25), 12.1% of PAN (4), 9.1% of PS (3), and 3% of PA-6 (1).

## 4. Discussion

### *4.1. Characterization and distribution of plastics in the Western Black Sea*

Being a primary hotspot for plastic pollution due to the Danube's freshwater influence, the Western Black Sea and the environs of the Danube Delta were identified to have the highest abundance in plastic particles (16–19 particles/m$^3$), whereas the southern sampling sites revealed lower concentrations (2.7–10.3 particles/m$^3$). The decrease in plastic particle concentration from the Danube Delta to the south along the Black Sea inner shelf has been confirmed by the balanced ANOVA and the Tukey Honestly Significant Differences (HSD) test. However, the statistical analyses showed that plastic loads in the four nearshore regions did not differ from another.

The northernmost region is under the pressure of a relatively high Danube freshwater input, especially during the flood seasons (spring and autumn) (Stancik et al., 1988). Samples were collected in a period with low precipitations (August). Nevertheless, highest concentrations of plastics were identified nearby the Danube mouths (16.1–18.6 particles/m$^3$; SG01 & SU01), probably as a result of a high plastic transport via the river. Further to the east, the abundance of plastics is presumably decreasing due to the N to S currents (Shapiro, 2019).

The second area, located in front of the Gura Portitei resort, is characterized by moderate concentrations of plastics (1.3-3.3 particles/m$^3$; PO04 & PO01). A difference is observed in plastic morphology: foils and fragments are the most commonly encountered forms in the PO04 sample, while the northern samples are dominated by fibers. This pattern could be explained by differences in current regimes.

The harbor city of Constanta is one of the major ports of the Black Sea with a high frequency of ships and many touristic activities along the coast. For the environs of Constanta, Suaria et al. (2015) reported that almost 90% of all findings floating on the surface were plastic waste. Surprisingly, in this 3rd area (CT01 & TZ18), the amount of plastics detected nearby urbanized areas is lower than in the environs of the Danube influence area (3–6 particles/m$^3$). Although several coastal areas north of Constanta are framed in protected natural areas, there was no difference in plastic load when compared to nearshore regions close to the cities Constanta and Mangalia. This might be explained by the wind regime, sea surface currents and wave movements (Shapiro, 2019) and shows how widespread plastic particles were. Nevertheless, in the study area, the surface currents may cause a north to south movement of the litter, with a transport of particles along the shore that implies an accumulation of Danube sourced plastics on Romanian and Bulgarian shores and in coastal surface waters (Berov and Klayn, 2020).

Closer to the Bulgarian border, the 4th region has been identified with high quantities of plastics (7.3–10.3 particles/m$^3$; MA05 & MA08). The increased plastic pollution close to the Bulgarian border is likely caused by litter input from Mangalia harbor or tourist resorts, indicated by the high abundance of fragments and plastic pieces found at the southernmost MA05 and MA08 sampling locations. It can be assumed that the influence of the Danube River is still visible at the southernmost locations which is indicated by some alike particles with same color/morphological characteristics as in samples from northern locations. The limited number of samples only gives first insights into the plastic pollution of the Western Black Sea. More detailed information about plastics in surface water will be obtained with a larger sampling network. This might help to develop further models of source to sink paths of plastics and, especially, will provide information on their land-based sources. Mesoplastics were surprisingly only found in two samples, close to the coast of Mangalia and in the nearshore region in the proximity of the Danube Delta. The current regime of the Black Sea, generally described as counterclockwise (Oguz et al., 1993), is responsible for a high dissemination rate of plastics and pollutants. The particle abundance can also be associated with surface currents of the Western Black Sea, described as a principally north-south movement, subsidiary eddy-like currents, of both water body and floating particles. For the Romanian coast eddy-like currents were described (Korotaev et al., 2003; Stănică and Chuturkova, 2007) that influence the distribution pattern of plastics in areas close to the coast.

Foils were identified in low amounts, with local exceptions (PO04: 47.6% foils; MA05: 22.7% foils; SG04: 19.3%). These particular anomalies could occur as a result of the eddy currents' presence (plausible in areas within a distance of 0–3 km from the shore, MA05), due to the presence of upwelling phenomena (Mihailov et al., 2012) or anthropogenic factors such as oil platforms present nearby sample location PO04.

Although only few particles have been measured with FTIR and pyrolysis GC-MS, a representative selection of types and colors has been analyzed. The results reveal a high abundance of the low-density polymers PP (density 0.89–0.91 g cm$^{-3}$) and PE (density 0.93–0.98 g cm$^{-3}$) (Avio et al., 2017). PP and PE easily float on the

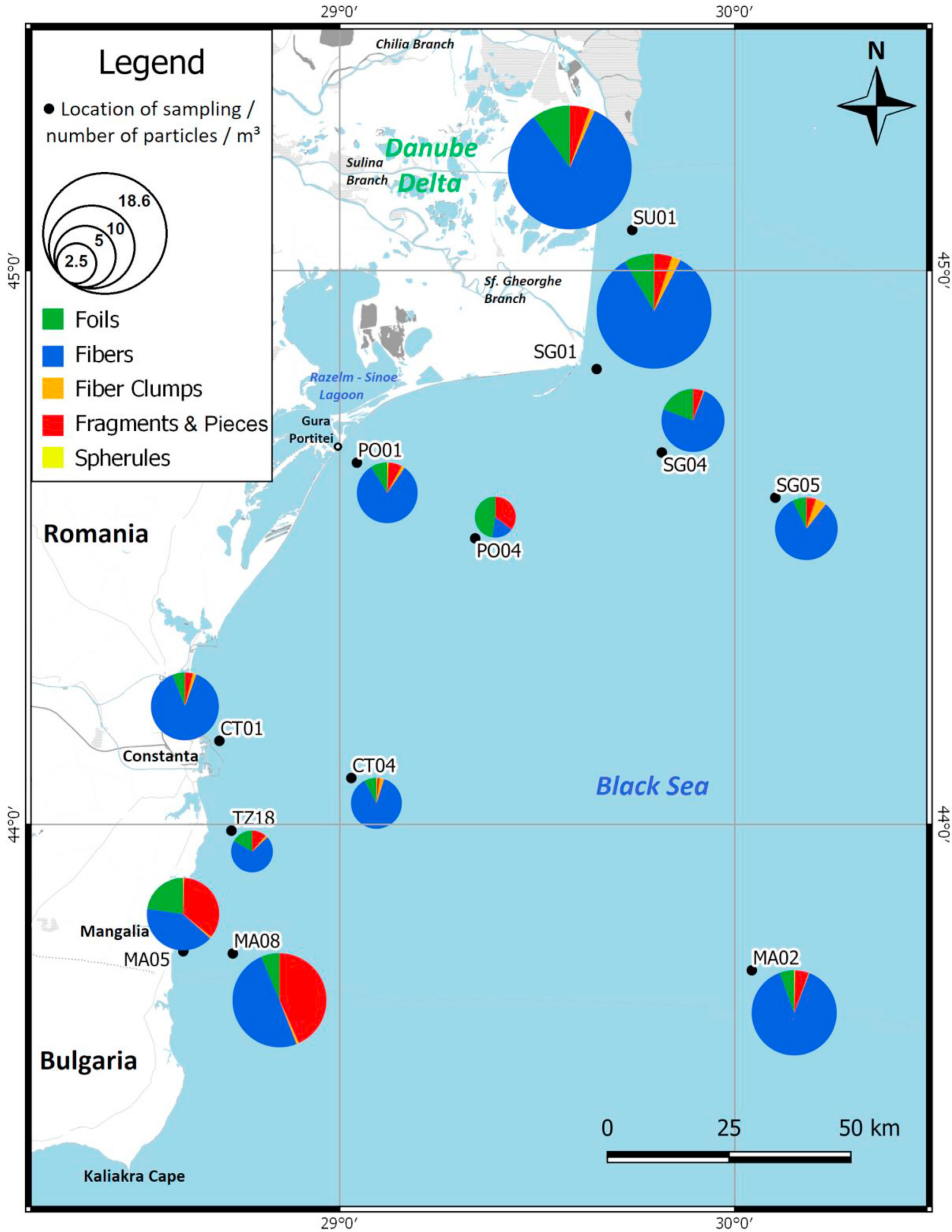


**Fig. 6.** Distribution of plastics in the western Black Sea at the locations near the Danube river mouth, at the four nearshore regions and at the two unreplicated locations.

water surface and are the most produced polymers worldwide (PlasticsEurope, 2019). This has been confirmed by other studies in Europe, e.g. the River Elbe, Germany (Scherer et al., 2020), Antuã River, Portugal (Rodrigues et al., 2018), a tributary of the Thames River, Great Britain (Horton et al., 2017) and Qin River, China (Zhang et al., 2020).

Supplementary visual discrimination of plastics (see supplement S3) reflects the abundance of the observed colors. The predominant particles are represented by black (46.6%), followed by white (24.6%) and blue (16%).

### 4.2. Differences between the Danube Delta and the city of Constanta

The main difference in particle morphology between the northern and eastern study area and the southern area close to the shore and Constanta (especially MA05 and MA08) are represented by the differences in concentration of fibers vs. fragments (see Fig. 6). While areas of high influence of the Danube (like those in front of the Delta and further south, south-east) are characterized by fibers as a major component of plastics, nearshore samples from the southern study area (TZ18, MA05 and MA08) reveal higher percentages of fragments, pieces and foils that might derive from land-based sources (e.g. tourism resorts, harbors). Regarding the polymer characterization of particles, a higher concentration of PP was observed in the northern area (SU, SG, PO, CT) and a higher polymer diversity in the southern region (TZ and MA), composed mainly of PE.

### 4.3. Sources

In the countries surrounding the Black Sea, Jambeck et al. (2015) estimated that up to 1 million tons of mismanaged plastic waste could be entering the Black Sea from all surrounding countries. Sources of plastics are most often land-based originating either from urban areas, rivers, sewage or tourism along the coasts (Wang et al., 2018). Thus, populated areas along the Black Sea shore are possible sources (Volckaert et al., 2012; ARCADIS, 2013). Especially mismanaged waste and dumping along the coast and in the sea were mentioned by several authors (Topçu et al., 2013; UNEP, 2005). From 1996 to 2005 marine litter input decreased in marine and coastal areas (UNEP, 2009). However, in the report it is also mentioned that solid waste from landfills may be released spontaneously into the sea and contributes to a growth in marine litter. UNEP (2009) listed primary sources of marine litter in Romania including municipal garbage/sewage, followed by fishery, marine transport, recreational activities along the coast, ports and industry.

Constanta is one of the most important harbors in Romania (Suaria et al., 2015). Most of the ships directly come to the port via the Mediterranean Sea (Davis, 2018). Thus, the most abundant ship traffic occurs south/southeast of the city and close to Mangalia.

Another important factor for plastic input is the Danube River. Topçu et al. (2013) reported that plastics were the dominant macrodebris in the Black Sea (ca. 47%), potentially originating from riverine inputs. Via the Danube River Delta, several tons of plastic waste are transported into the Black Sea every year. Only some studies are available. Lechner et al. (2014) detected an average of ca. 316 plastics per 1000 $m^3$ for the Austrian Danube between Vienna and Bratislava (500 μm net used). The majority of items originated from the industry (pellets, flakes and spherules). The authors estimated a plastic input into the Black Sea of ca. 4.2 t per day, thus ca. 1500 t per year. However, van der Wal et al. (2014) only estimates an input of up to 500 t per year, mainly due to the input of the River Siret. Lebreton et al. (2017) took into account 184 dams along the stretch of the Danube. Unfortunately, the origin of plastics in our study was not identifiable. Therefore, a reliable identification of the input sources of plastics was not possible. However, we assume that the PP fibers that dominated our samples could have derived from commonly used PP ropes (Welden and Cowie 2017).

Regarding plastic morphology, most of the particles were identified as fibers (74.6%), confirming the idea that fibers float for a longer period (de Haan et al., 2019). Fibers usually have a lower settling velocity than other plastic forms. This has been shown by Waldschläger and Schüttrumpf (2019) and Khatmullina and Isachenko (2017) for freshwater and by Bagaev et al. (2017) for the marine environment. Fibers may either derive from e.g. clothing or ropes (such as the analyzed PP fibers) and may originate from wastewater or shipping activities (Hidalgo-Ruz et al., 2012).

Considering the most abundant morphology of particles (fibers and foils), we assume that primary plastic objects that could be considered as generating sources of micro- and mesoplastics are black/white plastic bags and textiles. This is supported by the fact that larger particles (mesoplastics) were chemically identified as PE – the primary polymer used in manufacturing plastic bags.

Furthermore, some plastic particles close to the Danube Delta had different shapes than the plastic particles in the southernmost study area. It can be assumed that the missing plastic types either sank to the bottom of the sea due to biofouling (Wang et al., 2016) or were concentrated on sandy shores as a result of the wind regime and nearshore eddy-like currents (Stănică and Chuturkova, 2007) which are present south of the Danube Delta.

### 4.4. Limitations

A limitation of this study is the identification of analyzed particles. Only 2.83% tentative plastics were measured by means of ATR-FTIR and pyrolysis GC-MS with verification as polymers of 75%. An overestimation of tentative plastics is therefore well probable. However, the measured particles were chosen on the basis of representability of forms and colors. In future studies, more measurements have to be conducted.

### 4.5. Comparison with other studies

Few data about plastics in the Black Sea exist until present. Aytan et al. (2016) investigated microplastics in zooplankton samples with a 200 μm net and found predominantly fibers in the samples (between 600 and 1200 microplastics/$m^3$), many more than in our study. However, this is in line with our finding of a large abundance of fibers in the samples. Aytan et al. (2016) counted the particles with a binocular and did not verify them analytically. Thus, an overestimation is well probable. Öztekin and Bat (2017) investigated the southern Black Sea and found more microplastics in the water column (24 ± 26 microplastics/$m^3$) than on the water surface (~2.7 ± 2.3 microplastics/$m^3$). Only particles >300 μm were included in this study. The findings are lower than the ones in our study (1–19 microplastics/$m^3$) which can be explained by the larger mesh size.

Via the Bosporus, the Black Sea is connected with the Mediterranean Sea where many microplastic studies have been conducted. In few studies, nets with a mesh size of 200 μm were used. Therefore, the results are difficult to compare. Only studies in the Ligurian Sea, Western Sardinia and Ligurian and Sardinian Sea were conducted with 200 μm nets. Concentrations of 0.31 ± 1.17, 0.17 ± 0.32 and 0.62 ± 2 microplastics/$m^3$ were found, respectively (Fossi et al., 2012, 2016; Panti et al., 2015). Other studies (net mesh size: 333 μm) in the Mediterranean also revealed low concentrations of ~0.116 particles/$m^3$ (Collignon et al., 2012).

Other river deltas may also be compared to our study. Simon-Sánchez et al. (2019) sampled the Ebro Delta with a 5 μm net.

Fibers were the most abundant form, but microplastic concentrations were low (3.5 ± 1.4 microplastics/$m^3$). Zhao et al. (2014) studied the Yangtze estuary with a 333 μm net and found large differences between the estuary (4137.3 ± 2461.5 particles/$m^3$) and the sea (0.167 ± 0.138 particles/$m^3$). Therefore, it is possible that a large part of microplastics remains in the estuary and is deposited on the river banks or found in sediments (González et al., 2016).

## 5. Conclusion

In order to fill the gap and to contribute to the knowledge on plastic pollution, this study presents a first account of abundance and composition of plastic particle concentrations in surface waters of the Western Black Sea, in the eastern environs of the Danube Delta and along the Romanian and Bulgarian coasts. The results reveal plastic concentrations (micro- and mesoplastic) of surface waters with 1–19 particles/$m^3$ and an average concentration of 7 particles/$m^3$ across 12 study sites. The most dominant forms were fiber and fiber clumps (76.1%), followed by foils (12.7%), fragments (11.1%) and spherules (0.1%). PP and PE were the most abundant polymer types, confirming the hypothesis that low-density polymers mostly float on the water surface.

The results suggest that PE foils (including the mesoplastics) may originate from plastic bags while PP fibers may derive from ropes and fishing nets.

The highest plastic abundances occurred close to the mouth of the Danube River, probably originating from the Lower Danube basin. The concentrations south of the Delta and along the coast were significantly lower and revealed no significant difference between the four analyzed nearshore regions. Thus, it can be assumed that high amounts of the plastic are transported via the Danube River into the Black Sea. It is anticipated to have surmises regarding the source to sink approach and transport pathways that could improve uncertain models of the plastic particles' fate in the aquatic environments. Considering the limited number of sampling sites, we suggest to continue analyzing the studied area taking into account a more complex sampling network. This study provides insights into plastic pollution of the relatively understudied Black Sea and showed that more plastic particles are present in the Western Black Sea, especially in the eastern environs of the Danube Delta, compared to other studies of the Black and the Mediterranean Sea.

## CRediT author statement

**IP:** Conceptualization, Methodology, Writing - Original Draft, Supervision. **CK:** Investigation, Visualisation, Writing – Review & Editing, Data Curation. **GD:** Investigation, Data Curation. **SME:** Investigation, Data Curation, Formal Analysis, Writing – Review & Editing. **GR:** Writing – Review & Editing, Resources, Validation. **FS:** Investigation, Validation, Writing – Review & Editing.

## 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.

## Acknowledgements

This study was financially supported by the Romanian Ministry of Education and Research projects: Grant No. 8PFE/2018 – FLUVIMAR and National Core Program projects for Black Sea shelf monitoring - Grant no. PN19/20 and by EC H2020 Grant No. 739562 – DANUBIUS PP. We thank Cornel Ioan Pop (GeoEcoMar) for support in designing the maps.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.115724.

## References

Akbal, F., Gurel, L., Bahadir, T., Guler, I., Bakan, G., Buyukgungor, H., 2011. Water and sediment quality assessment in the mid-Black Sea coast of Turkey using multivariate statistical techniques. Environ. Earth Sci. 64, 1387–1395.

ARCADIS, 2013. Final Report. Pilot Project 4 Seas: Case Studies on the Plastic Cycle and its Loopholes in the Four European Regional Seas Areas. European Commission, project number BE011102328.

Arthur, C., Baker, J., Bamford, H., 2009. Proceedings of the International Research Workshop on the Occurrence, Effects, and Fate of Microplastic Marine Debris, vol. 30. NOAA Technical Memorandum NOS-OR&R-, pp. 1–49.

Avio, C.G., Gorbi, S., Regoli, F., 2017. Plastics and microplastics in the oceans: from emerging pollutants to emerged threat. Mar. Environ. Res. 128, 2–11.

Aytan, U., Esensoy, F., Senturk, Y., 2018. Microplastic ingestion by calanoid copepods in the SE Black Sea. In: Baztan, J., Bergmann, M., Carrasco, A., Fossi, M.C., Jorgensen, B., Miguelez, A., Pahl, S., Thompson, R.C., Vanderlinden, J.-P. (Eds.), MICRO 2018 Fate and Impact of Microplastics: Knowledge, Actions and Solutions.

Aytan, U., Valente, A., Senturk, Y., Usta, R., Esensoy Sahin, F.B., Mazlum, R.E., Agirbas, E., 2016. First evaluation of neustonic microplastics in Black Sea waters. Mar. Environ. Res. 119, 22–30.

Bagaev, A., Mizyuk, A., Khatmullina, L., Isachenko, I., Chubarenko, I., 2017. Anthropogenic fibres in the Baltic Sea water column: field data, laboratory and numerical testing of their motion. Sci. Total Environ. 599–600, 560–571.

Bakan, G., Büyükgüngör, H., 2000. The Black Sea. Mar. Pollut. Bull. 41, 24–43.

Bergmann, M., Wirzberger, V., Krumpen, T., Lorenz, C., Primpke, S., Tekman, M.B., Gerdts, G., 2017. High quantities of microplastic in arctic deep-sea sediments from the HAUSGARTEN observatory. Environ. Sci. Technol. 51, 11000–11010.

Berov, D., Klayn, S., 2020. Microplastics and floating litter pollution in Bulgarian Black Sea coastal waters. Mar. Pollut. Bull. 156, 111225.

Besseling, E., Redondo-Hasselerharm, P., Foekema, E.M., Koelmans, A.A., 2018. Quantifying ecological risks of aquatic micro- and nanoplastic. Crit. Rev. Environ. Sci. Technol. 49 (1), 32–80.

Blettler, M., Abrial, E., Khan, F., Sivri, N., Espínola, L., 2018. Freshwater plastic pollution: recognizing research biases and identifying knowledge gaps. Water Res. 143 (15), 416–424.

BSC, 2007. Marine litter in the Black Sea Region: A review of the problem. Black Sea Commission Publications 2007-1, Yazılım ve Yayıncılık. Ltd., Istanbul, Turkey, pp. 160–pp.

Collignon, A., Hecq, J.-H., Glagani, F., Voisin, P., Collard, F., Goffart, A., 2012. Neustonic microplastic and zooplankton in the north western Mediterranean Sea. Mar. Pollut. Bull. 64, 861–864.

Crawford, C.B., Quinn, B., 2017. 4-Physiochemical properties and degradation. Microplastic Pollutants. Elsevier, pp. 57–100.

Davis, D.K., 2018. Between sand and sea: constructing Mediterranean plant ecology. In: The Palgrave Handbook of Critical Physical Geography, vols. 129–151. Palgrave Macmillan, Cham.

de Haan, W.P., Sanchez-Vidal, A., Canals, M., 2019. Floating microplastics and aggregate formation in the western Mediterranean Sea. Mar. Pollut. Bull. 140, 523–535.

de Souza Machado, A.A., Lau, C.W., Till, J., Kloas, W., Lehmann, A., Becker, R., Rillig, M.C., 2018. Impacts of microplastics on the soil biophysical environment. Environ. Sci. Technol. 52, 9656–9665.

Dierkes, G., Lauschke, T., Becher, S., Schumacher, H., Földi, C., Ternes, T., 2019. Quantification of microplastics in environmental samples via pressurized liquid extraction and pyrolysis-gas chromatography. Anal. Bioanal. Chem. 411 (26), 6959–6968.

Duliu, O.G., Cristache, C., Oaie, G., Culicov, O.A., Frontasyeva, M.V., Toma, M., 2009. ENAA Studies of pollution in anoxic Black Sea sediments. Mar. Pollut. Bull. 58, 827–831.

Ehlers, S.M., Manz, W., Koop, J.H.E., 2019. Microplastics of different characteristics are incorporated into the larval cases of the freshwater caddisfly *Lepidostoma basale*. Aquat. Biol. 28, 67–77.

FAO, 2015. Global Forest Resources Assessment. UN Food and Agriculture Organization, Rome. FAO Forestry Paper No. 1⁄.

Fossi, M.C., Marsili, L., Baini, M., Giannetti, M., Coppola, D., Guerranti, C., Caliani, I., Minutoli, R., Lauriano, G., Finoia, M.G., Rubegni, F., Panigada, S., Bérubé, M., Urbán Ramírez, J., Panti, C., 2016. Fin whales and microplastics: the Mediterranean Sea and the sea of cortez scenarios. Environ. Pollut. 209, 68–78.

Fossi, M.C., Panti, C., Guerranti, C., Coppola, D., Giannetti, M., Marsili, L., Minutoli, R., 2012. Are baleen whales exposed to the threat of microplastics? A case study of the Mediterranean fin whale (*Balaenoptera physalus*). Mar. Pollut. Bull. 5864, 2374–2379.

GESAMP, 2019. Guidelines for the monitoring and assessment of plastic litter and microplastics in the ocean. Rep. Stud. GESAMP No. 99, 130.

González, D., Hanke, G., Tweehuysen, G., Bellert, B., Holzhauer, M., Palatinus, A., Hohenblum, P., Oosterbaan, L., 2016. Riverine litter monitoring - options and recommendations. MSFD GES TG Marine Litter Thematic Report,. JRC Technical Report, EUR 28307.
He, D., Luo, Y., Lu, S., Liu, M., Song, Y., Lei, L., 2018. Microplastics in soils: analytical methods, pollution characteristics and ecological risks. Trends Anal. Chem. 109, 163–172.
Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., Thiel, M., 2012. Microplastics in the marine environment: a review of the methods used for identification and quantification. Environ. Sci. Technol. 46, 3060–3075.
Horton, A.A., Svendsen, C., Williams, R.J., Spurgeon, D.J., Lahive, E., 2017. Large microplastic particles in sediments of tributaries of the River Thames, UK – abundance, sources and methods for effective quantification. Mar. Pollut. Bull. 114, 218–226.
Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. Science 347, 768–771.
Khatmullina, L., Isachenko, I., 2017. Settling velocity of microplastic particles of regular shapes. Mar. Pollut. Bull. 114, 871–880.
Korotaev, G., Oguz, T., Nikiforov, A., Koblinsky, C., 2003. Seasonal, interannual, and mesoscale variability of the Black Sea upper layer circulation derived from altimeter data. J. Geophys. Res. Oceans 108, C4.
Lebreton, L.C.M., van der Zwet, J., Damsteeg, J.-W., Slat, B., Andrady, A., Reisser, J., 2017. River plastic emissions to the world's oceans. Nat. Commun. 8, 15611.
Lechner, A., Keckeis, H., Lumesberger-Loisl, F., Zens, B., Krusch, R., Tritthart, M., Glas, M., Schludermann, E., 2014. The Danube so colourful: a potpourri of plastic litter outnumbers fish larvae in Europe's second largest river. Environ. Pollut. 188, 177–181.
Lehmann, A., Giuliani, G., Mancosu, E., Abbaspour, K.C., Sözen, S., Gorgan, D., Beel, A., Ray, N., 2015. Filling the gap between Earth observation and policy making in the Black Sea catchment with enviroGRIDS. Environ. Sci. Pol. 46, 1–12.
Luo, W., Su, L., Craig, N.J., Du, F., Wu, C., Shi, H., 2019. Comparison of microplastic pollution in different water bodies from urban creeks to coastal waters. Environ. Pollut. 246, 174–182.
Mai, L., Bao, L.-J., Shi, L., Wong, C.S., Zeng, E.Y., 2018. A review of methods for measuring microplastics in aquatic environments. Environ. Sci. Pollut. Res. 25, 11319–11332.
Mani, T., Blarer, P., Storck, F.R., Pittroff, M., Wernicke, T., Burkhardt-Holm, P., 2019. Repeated detection of polystyrene microbeads in the lower Rhine river. Environ. Pollut. 245, 634–641.
Mihailov, M.E., Tomescu-Chivu, M.I., Dima, V., 2012. Black Sea water dynamics on the Romanian littoral – case study: the upwelling phenomena. Rom. Rep. Phys. 64, 232–245.
Moncheva, S., Stefanova, K., Krastev, A., Apostolov, A., Bat, L., Sezgin, M., Sahin, F., Timofte, F., 2016. Marine litter quantification in the Black Sea: a pilot assessment. Turk. J. Fish. Aquat. Sci. 16, 213–218.
Norén, F., 2007. Small plastic particles in Coastal Swedish waters. KIMO Sweden, p. 11.
Oguz, T., Latun, V.S., Latif, M.A., Vladimirov, V.V., Sur, H.I., Markov, A.A., Özsoy, E., Kotovshchikov, B.B., Eremeev, V.V., Ünlüata, Ü., 1993. Circulation in the surface and intermediate layers of the Black Sea. Deep-Sea Res. Part I Oceanogr. Res. Pap. 40, 1597–1612.
Ozkoc, H.B., Bakan, G., Ariman, S., 2007. Distribution and bioaccumulation of organochlorine pesticides along the Black Sea coast. Environ. Geochem. Health 29, 59–68.
Öztekin, A., Bat, L., 2017. Microlitter pollution in sea water: a preliminary study from Sinop Sarikum coast of the southern Black Sea. Turk. J. Fish. Aquat. Sci. 17, 1431–1440.
Panti, C., Giannetti, M., Baini, M., Rubegni, F., Minutoli, R., Fossi, M., 2015. Occurrence, relative abundance and spatial distribution of microplastics and zooplankton NW of Sardinia in the Pelagos Sanctuary Protected Area, Mediterranean Sea. Environ. Chem. 12.
Peng, G., Xu, P., Zhu, B., Bai, M., Li, D., 2018. Microplastics in freshwater river sediments in Shanghai, China: a case study of risk assessment in mega-cities. Environ. Pol. 234, 448–456.
PlasticsEurope, 2019. Plastics - the Facts 2019: an Analysis of European Plastics Production, Demand and Waste Data.
Popa, M., Morar, D., Adrian, T., Teuşdea, A., Popa, D., 2014. Study concerning the pollution of the marine habitats with the microplastic fibres. J. Environ. Prot. Ecol. 15, 916–923.
Prata, J.C., da Costa, J.P., Duarte, A.C., Rocha-Santos, T., 2019. Methods for sampling and detection of microplastics in water and sediment: a critical review. Trends Anal. Chem. 110, 150–159.
Rodrigues, M.O., Abrantes, N., Gonçalves, F.J.M., Nogueira, H., Marques, J.C., Gonçalves, A.M.M., 2018. Spatial and temporal distribution of microplastics in water and sediments of a freshwater system (Antuã River, Portugal). Sci. Total Environ. 633, 1549–1559.
Sarı, E., Çağatay, M.N., Acar, D., Belivermiş, M., Kılıç, Ö., Arslan, T.N., Tutay, A., Kurt, M.A., Sezer, N., 2018. Geochronology and sources of heavy metal pollution in sediments of Istanbul Strait (Bosporus) outlet area, SW Black Sea, Turkey. Chemosphere 205, 387–395.
Scherer, C., Weber, A., Stock, F., Vurusic, S., Egerci, H., Kochleus, C., Arendt, N., Foeldi, C., Dierkes, G., Wagner, M., Brennholt, N., Reifferscheid, G., 2020. Microplastics in the water and sediment phase of the Elbe river, Germany. Sci. Total Environ. 738, 139866.
Schwarz, A.E., Ligthart, T.N., Boukris, E., van Harmelen, T., 2019. Sources, transport, and accumulation of different types of plastic litter in aquatic environments: a review study. Mar. Pollut. Bull. 143, 92–100.
Shapiro, G.I., 2019. Black Sea circulation. In: Cochran, J.K., Bokuniewicz, H.J., Yager, P.L. (Eds.), Encyclopedia of Ocean Sciences, third ed. Academic Press, Oxford, pp. 303–317.
Siegfried, M., Koelmans, A.A., Besseling, E., Kroeze, C., 2017. Export of microplastics from land to sea. A modelling approach. Water Res. 127, 249–257.
Simeonova, A., Chuturkova, R., 2019. Marine litter accumulation along the Bulgarian Black Sea coast: categories and predominance. Waste Manag. 84, 182–193.
Simon-Sánchez, L., Grelaud, M., Garcia-Orellana, J., Ziveri, P., 2019. River Deltas as hotspots of microplastic accumulation: the case study of the Ebro River (NW Mediterranean). Sci. Total Environ. 687, 1186–1196.
Stănică, A., Chuturkova, R., 2007. Coastal changes at the Sulina mouth of the Danube River as a result of human activities. Mar. Pollut. Bull. 55, 555–563.
Stock, F., Kochleus, C., Bänsch-Baltruschat, B., Brennholt, N., Reifferscheid, G., 2019. Sampling techniques and preparation methods for microplastic analyses in the aquatic environment – a review. Trends Anal. Chem. 113, 84–92.
Suaria, G., Melinte-Dobrinescu, M.C., Ion, G., Aliani, S., 2015. First observations on the abundance and composition of floating debris in the North-western Black Sea. Mar. Environ. Res. 107, 45–49.
Topçu, E.N., Tonay, A.M., Dede, A., Öztürk, A.A., Öztürk, B., 2013. Origin and abundance of marine litter along sandy beaches of the Turkish Western Black Sea Coast. Mar. Environ. Res. 85, 21–28.
Triebskorn, R., Braunbeck, T., Grummt, T., Hanslik, L., Huppertsberg, S., Jekel, M., Knepper, T.P., Krais, S., Müller, Y.K., Pittroff, M., Ruhl, A.S., Schmieg, H., Schür, C., Strobel, C., Wagner, M., Zumbülte, N., Köhler, H.-R., 2019. Relevance of nano- and microplastics for freshwater ecosystems: a critical review. Trends Anal. Chem. 110, 375–392.
Tsuge, S., Ohtani, H., Watanabe, C., 2011. Pyrolysis-GC/MS Data Book of Synthetic Polymers. Elsevier B.V.
Tuncer, G., Karakas, T., Balkas, T.I., Gökçay, C.F., Aygnn, S., Yurteri, C., Tuncel, G., 1998. Land-based sources of pollution along the black sea coast of Turkey: concentrations and annual loads to the black sea. Mar. Pollut. Bull. 36, 409–423.
UNEP, 2005. Marine Litter: an Analytical Overview. UNEP, pp. 1–47.
UNEP, 2009. Marine Litter: A Global Challenge, p. 232.
van der Wal, M., van der Meulen, M., Tweehuijsen, G., Peterlin, M., Palatinus, A., Kovač Viršek, M., Coscia, L., Kržan, A., 2014. SFRA0025: Identification and Assessment of Riverine Input of (Marine) Litter, pp. 1–172. Final Report for the European Commission DG Environment under Framework Contract No ENV.D.2/FRA/2012/0025 – Consultation Draft.
Volckaert, A., Vanacoleyen, M., Perez, C., Cools, J., Mira Veiga, J., 2012. Pilot Project '4 Seas'– Plastic Recycling Cycle and Marine Environmental Impact: Case Studies on the Plastic Cycle and Its Loopholes in the Four European Regional Seas Areas. European Commission Project number BE011102328.
Wagner, M., Lambert, S., 2018. Freshwater Microplastics: Emerging Environmental Contaminants. Springer International Publishing, Cham.
Waldschläger, K., Schüttrumpf, H., 2019. Effects of particle properties on the settling and rise velocities of microplastics in freshwater under laboratory conditions. Environ. Sci. Technol. 53, 1958–1966.
Wang, J., Zheng, L., Li, J., 2018. A critical review on the sources and instruments of marine microplastics and prospects on the relevant management in China. Waste Manag. Res. 36, 898–911.
Wang, J., Tan, Z., Peng, J., Qiu, Q., Li, M., 2016. The behaviors of microplastics in the marine environment. Mar. Environ. Res. 113, 7–17.
Welden, N.A., Cowie, P.R., 2017. Degradation of common polymer ropes in a sublittoral marine environment. Mar. Pollut. Bull. 118 (1–2), 248–253.
Zhang, L., Liu, J., Xie, Y., Zhong, S., Yang, B., Lu, D., Zhong, Q., 2020. Distribution of microplastics in surface water and sediments of Qin river in Beibu Gulf, China. Sci. Total Environ. 708, 135176.
Zhao, S., Zhu, L., Wang, T., Li, D., 2014. Suspended microplastics in the surface water of the Yangtze Estuary System, China: first observations on occurrence, distribution. Mar. Pollut. Bull. 86, 562–568.