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Plastic debris in the Mediterranean Sea: Types, occurrence and distribution along Adriatic shorelines

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ABSTRACT

Small plastic debris in sediments from five beaches were investigated to evaluate their occurrence and abundance in the Northern Adriatic coast for the first time. Plastic debris extracted from sediments were counted, weighted and identified by Fourier-transform infrared spectroscopy (FT-IR). A total of 1345 items of debris (13.491 g) were recorded, with a mean density of 12.1 items kg^{-1} d.w. and 0.12 g kg^{-1} d.w. Fragments were the most frequent type of small plastics debris detected. In terms of abundance, microplastics (<5 mm) accounted for 61% of debris, showing their wide distribution on Adriatic coasts, even far-away from densely populated areas. The majority of the polymers found were polyolefins: there were greater quantities of polyethylene and polypropylene compared to other types of plastic. Primary microplastics accounted for only 5.6% of the total plastic debris. There were greater quantities of microplastics at sites subjected to stronger riverine runoff. The results will provide useful background information for further investigations to understand the sink and sources of this emergent and priority contaminant.

1. Introduction

Plastics are essential in our everyday lives. World production of plastics has strongly expanded, from 1.7 million tonnes in 1950 to 322 million tonnes in 2015 (Plastic Europe, 2016). Whether deliberately or accidently, when plastics waste is not properly disposed it may end up as litter in the environment, seas and rivers and harming wild life, fisheries and tourism. Through a combination of photodegradation, oxidation and mechanical abrasion, the degradation rate of plastics in the environment is slow and results in production of small fragments and microplastics (Barnes et al., 2009). The existence of microplastics (plastic particulates < 5 mm; Ivar do Sul and Costa, 2014) in the marine environment has been known for nearly half a century (Carpenter and Smith, 1972). While pictures of macroplastic debris in ocean gyres (Moore et al., 2001) and of the excessive accumulation of litter on beaches in the most remote locations worldwide (e.g. Convey et al., 2002; Foster-Smith et al., 2007) have fostered the awareness of plastic pollution, microplastics 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 (Claessens et al., 2011; Ivar do Sul and Costa, 2014).

The most widely used plastics are polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET), which represent grossly 90% of the total world production (Andrady and Neal, 2009). Millions of tonnes of plastic waste (4.8–12.7 million tonnes in 2010) end up the marine environment (Jambeck et al., 2015). Certain plastics are expected to occur in greater abundances than others due to the relative proportions that are manufactured, used, and discarded. For instance, half of all the plastics that are produced annually are polyolefins, i.e. PE and PP (Plastic Europe, 2016), which are principally used to make packaging that is used once and then discarded. It is, however, not known whether polyolefins occur in greater abundance as items of debris compared to other polymers. The most prominent types of microplastics identified in the marine environment include pellets, irregular fragments, films and fibers (Wright et al., 2013) of which can be classified as primary or secondary microplastics. Primary microplastics are intentionally produced as precursors to other products, while secondary microplastics result from the degradation of macroplastics due to chemical, mechanical and photolytic degradation processes in the marine environment (Mathalon and Hill, 2014). The sources of primary microplastics are usually plastic pellet processing facilities at

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petrochemical plants, and specific trading activities such as oceanic shipping routes (Thompson et al., 2009). Small sized primary microplastics granules are also present in cosmetics products and used as abrasives in a wide range of applications (Browne, 2015).

The Marine Strategy Framework Directive, MSFD (2008/56/EC; European Commission, 2008) establishes a framework for each Member State to take action to achieve or maintain Good Environmental Status (GES) for the marine environment by 2020. The MSFD follows a holistic functional approach identifying a set of 11 Descriptors, which collectively represent the state and functioning of the whole system (Borja et al., 2010). Descriptor 10 (D10) is identified as "Properties and quantities of marine litter do not cause harm to the coastal and marine environment" (European Commission, 2008). Microplastics are considered specifically in descriptor 10 of the MSFD (10.1.3 "*Trends in the amount, distribution and, where possible, composition of micro-particles (in particular micro-plastics)*"), and implicitly in the indicator related with impacts of litter on marine life. According to the MSDF, microplastics should be categorized according to their physical characteristics including size and shape. It is also important to obtain information on polymer type (Gago et al., 2016).

The Adriatic Sea is characterized by one of the greatest seafloor litter pollution among Mediterranean regions (Pasquini et al., 2016). The north-western Adriatic coast is thus vulnerable to plastic accumulation on beaches from land sources due to river discharges, marine sources due to aquaculture, fishing and recreational maritime activities, as well as being an important route for commercial vessels and cruise ships. Abundant scientific literature has extensively explored the various anthropogenic impacts affecting this fragile coastal ecosystem (Munari et al., 2011; Torresan et al., 2012; Romano and Zullo, 2014), but the presence and diffusion of microplastics as contaminants have not yet been investigated in any environmental compartment.

With the present study we wanted to assess, for the first time in the north-western Adriatic coast, the quality and quantity of small plastic debris occurring in beach sediments to address the gap in knowledge and to serve as a baseline for future comparisons. Further hypotheses tested were that: (1) microplastics will be found in greater numerical abundance than macroplastic debris; (2) PE and PP will be more abundant than other polymers due to differences in levels of production; (3) the amount of primary microplastics will be prevalent respect to secondary microplastics because of nearby petrochemical industrial parks (Marghera, Ferrara, Ravenna); (4) there will be differences in microplastics abundance between beaches with strong riverine inputs and those with weak riverine inputs. We considered beach sediments at the high water line, since they reflect the amount of microplastics washed towards the coastlines with the tidal flows (Martins and Sobral, 2011).

2. Methods

2.1. Study area

Along the north-western Adriatic coast a large number of rivers discharge into the sea, being the Po River the most relevant, followed by the Adige. Five beaches (Fig. 1), differently affected by riverine runoff, were sampled. The considered area is subjected to intense marine traffic from supplier vessels for offshore activities (gas platforms), trawl-fishing vessels, and recreational boats. It is also an area of intense aquaculture, with offshore mussel farms, and coastal clam cultivations. Inland, a few dozen kilometers away from the sampled beaches, there are three important petrochemical industrial parks: Porto Marghera, Ferrara, and Ravenna.

2.2. Sampling and analysis

Beach surveys were conducted at the 5 beaches in May 2015. At each beach there were two replicate sites separated by 200 m. Each site consisted of a 10 m stretch of linear shoreline. At each site, sampling was performed by using quadrats placed along the last high tide mark, as plastic is preferably accumulated in this zone (Martins and Sobral, 2011). Three replicate samples were collected at each site by scraping the first 5 cm of sand from 50×50 cm quadrats (Galgani et al., 2011; Martins and Sobral, 2011; Jayasiri et al., 2013). Replicates of the same site were separated by 5 m. All samples were obtained during calm conditions with low wave activity. Samples were placed in labelled bags and transferred to the laboratory, where all replicates were analyzed separately.

In the laboratory, sediment samples were dried at 50 °C during 48 h. Each sediment sample was then divided into subsamples and the plastic debris 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 four groups: micro ($\leq$5 mm), meso (>5–20 mm), macro (>20–100 mm) and mega (>100 mm) (Jayasiri et al., 2013). Plastic debris were also categorized according to shape (i.e., fiber, film, fragment or pellet).

Fourier-transform infrared spectroscopy (FT-IR) analysis of 20 plastic debris for each shape type 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 self-collected, polymer reference library.

Differences in abundances of plastic debris (categorized by shape and dimension) were analyzed through permutational analysis of variance (PERMANOVA). The similarity matrix was calculated using the Bray-Curtis index and abundance data were log (x + 1) transformed. The experimental design incorporated two factors: "Location" (fixed) with 5 levels: Rosolina (ROS), Volano (VOL), Bellocchio (BEL), Casalborsetti (CAS) and Bevano (BEV), and "Site" (random and nested within the factor "Location") with 10 levels: ROS1, ROS2, VOL1, VOL2, etc. Similarity percentage (SIMPER) analysis was used to explore differences in plastics distribution (categorized by dimension) within and between beaches. All statistical analyses were performed using PRIMER v.6 and its add-on package PERMANOVA+ (Anderson et al., 2008).

Data of river runoff was obtained by Regional Agencies Annual Reports (ARPAV, 2014; ARPA, 2015).

3. Results

Thirty quadrats were sampled at the five beaches. Some examples of plastic debris collected during the study are shown in Fig. 2. The smallest debris collected was 0.8 mm of length. All sediment samples collected on the beaches contained plastics. A total of 1345 items of debris (13.491 g) were recorded from the 30 samples of sediment, with a mean density of 12.1 items kg^{-1} d.w. and 0.12 g kg^{-1} d.w. The greatest plastic abundance by number and weight was observed at Volano (21.6 ± 12.8 items kg^{-1} d.w., and 0.28 ± 0.29 g kg^{-1} d.w., respectively). In contrast, the lowest mean values by number and weight were 5.99 ± 3.25 items kg^{-1} d.w. and 0.013 ± 0.01 g kg^{-1} d.w. at Bellocchio.

As predicted there was greater abundance of smaller debris (micro and meso) compared to macro and mega plastic debris (Hypothesis 1). This was reflected in the frequency distribution of different sizes of debris, which were skewed toward smaller debris (Fig. 3). In terms of numerical abundance, microplastic

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