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Microplastic particles in sediments of Lagoon of Venice, Italy: First observations on occurrence, spatial patterns and identification



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ABSTRACT

In order to improve knowledge of the identification, distribution and abundances of microplastic particles of 1 mm or less (S-MPPs) in the coastal area of the Mediterranean region, a preliminary monitoring survey was carried out in a transitional environment along the north-eastern Italian coasts, the Lagoon of Venice. S-MPPs were evaluated in sediments collected from 10 sites chosen in shallow areas variously affected by natural conditions and anthropogenic influences (i.e., landward stations influenced by freshwater inputs, seaward areas near sea inlets, and sites influenced by the presence of aquaculture farms, industry and city centers). S-MPPs, extracted from bulk sediments by density separation, were counted and identified by Fourier-Transform Infrared Micro-spectroscopy (µFT-IR). The µFT-IR process included automatic surface chemical mapping and references to an infrared library database to identify the compositional spectra of particles. S-MPPs were recovered from all samples - a fact which emphasizes their extensive distribution throughout the Lagoon. Total abundances varied from 2175 to 672 S-MPPs kg⁻¹ d.w., higher concentrations generally being observed in landward sites. Of the ten polymer types identified, the most abundant, accounting for more than 82% of total S-MPPs, were polyethylene and polypropylene. The most frequent size (93% of observed microplastics) was in the range 30–500 μm. Total S-MPP values were significantly correlated with the finer sediment fraction and with the metal pollution index.

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1. Introduction

The worldwide production of synthetic organic polymers, called plastics, is now estimated to be greater than 250 million tons/year (Plastics Europe, 2012). The extent of production and increased use of disposable goods, together with poor rates of degradability, have all contributed to the environmental problem of plastic debris accumulating in natural habitats (Barnes et al., 2009). The long life and strength of plastics, estimated to be in the range of tens to hundreds of years, also contribute to the significant rise in plastic pollution. The occurrence and distribution of large amounts of plastic debris have been well documented, at least in the marine environment (for reviews, see Moore, 2008; Barnes et al., 2009). However, despite the durability of synthetic polymers, large plastic items eventually undergo fragmentation, mainly as a consequence of mechanical breakdown caused by wave action and

photochemical processes triggered by UV-B light (Corcoran et al., 2009; Cooper and Corcoran, 2010; Andrady, 2011). It has been suggested that smaller plastic fragments (basically ≤ 5 mm), previously categorized as microplastics by several authors (e.g., Gregory and Andrady, 2003; Moore, 2008) must be regarded either as large microplastic (L-MPP, range 1–5 mm) or small microplastic particles (S-MPP, ≤ 1 mm) (Imhof et al., 2012).

The widespread occurrence of microplastics in various marine and freshwater habitats worldwide is at present well documented, and has mainly been investigated in sandy beaches and coastal/ transitional sediments (Browne et al., 2010). Despite isolated regional surveys regarding mainly sandy beaches, estuarine and sub-tidal habitats, and marine sediments all over the world, data on the distribution and dispersion of microplastics in the Mediterranean are almost completely lacking. The only available study, reporting abundance values for microplastic particles floating in the water column, was recently carried out in the Tyrrhenian (Collignon et al., 2012). The need for more knowledge becomes even more evident when we consider that EU member states must develop activities to reach "good environmental status" in the

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marine environment by 2020, as stated in the Marine Strategy Framework Directive (Galgani et al., 2010).

The Lagoon of Venice is one of the largest Mediterranean transitional environments (surface area about 550 km²) and contains a variety of aquatic and terrestrial habitats such as marshes, tidal flats, canals, and islands, on which the two main cities of Venice and Chioggia and a number of smaller towns are located.

Abundant scientific literature over the years has extensively explored the various anthropogenic impacts affecting this fragile lagoon ecosystem, but the presence and diffusion of microplastics as contaminants have not yet been investigated in any environmental compartment. This is quite unexpected, in view of the many potential sources contributing to the presence of microplastics in the Lagoon. Some of the best-known sources are freshwater run-off from the drainage basin of 2000 km² and direct entry from eleven major and several minor tributaries, occasional industrial spillages from industries on the Lagoon borders producing polyvinylchloride (PVC), polyethylene terephthalate (PET), polyethylene (PE), polystyrene (PS) and polyamide raw pellets, debris from fishing nets, and industrial and urban discharges. New and quite specific sources may also be identified following the recent positioning of geotextile defenses at many sites in the shallower parts of the Lagoon (Cecconi, 2005) and the latest introduction of new, more durable, plastic materials progressively replacing the now degraded wooden piles, traditionally used for navigation and marking deep-waters along the canals, and for mooring boats along the banks.

This study has two main aims: to examine the presence and diffusion of S-MPPs in the sediments of the Lagoon of Venice, and to explore a new analytical approach, involving improvements in techniques for comparing the size, type and shape of plastic polymers, which may supply functional insights into the sources and distribution of isolated microplastic fragments. Micro-Fourier-Transform Infrared Spectroscopy (μ FT-IR), together with references to an infrared library database to classify particle spectra, were complemented with environmental scanning electron microscopy with energy-dispersive spectrometric imaging (ESEM-EDS), for further information on morphological and surface appearance.

2. Materials and methods

2.1. Study area and sediment sampling

Field sampling of sediments was designed for an initial overview of S-MPPs extending in the superficial sediments of the Lagoon of Venice and to pinpoint their main sources by identifying their chemical composition. Sites were selected according to

hydrodynamic conditions and environmental features, both natural and anthropogenic. The hydrodynamic of the Lagoon is linked to tides, water exchange with the sea through the three inlets, and riverine inputs (Gačić et al., 2002). The resulting general picture indicates that there is an energy-decreasing gradient from seaward to landward areas, mean current velocities falling from values of >30 cm s⁻¹ near the inlets to <6 cm s⁻¹ in the more internal areas (Molinaroli et al., 2007). However, the dominant winds in the northern Adriatic, mainly the NE "bora" and the SE "scirocco", sometimes significantly affect these water dynamics, which may be enhanced up to cause stream velocity at >100 cm s⁻¹, with a concurrent reduction in water residence times to less than 4 days (Cucco and Umgiesser, 2006; Gačić et al., 2009; Mancero-Mosquera et al., 2010). The inputs of S-MPPs into the Lagoon are tentatively attributed to urban discharges from Venice and Chioggia, with about 60,000 and 50,000 inhabitants, respectively, to run-off from the port and the industrial zone nearby (Porto Marghera), and to mussel/clam farming, which is widespread in all shallow waters. Land-originating anthropogenic materials, which are transferred to the Lagoon water/sediments by tributary rivers, may also convey microplastics or their precursors. Two of the main tributaries, the rivers Silone and Dese, account for 44% of the total freshwater inputs, and have been evaluated at about $16~\text{m}^3~\text{s}^{-1}$ as a yearly mean (Zonta et al., 2001).

The ten selected sampling sites are all located in shallow waters (average depth $<1\pm0.5$ m, varying with tide). Three of them include landward areas influenced by freshwater inputs and low water dynamics (1, Palude della Rosa; 7, Lago Rivolta; 8, Valle di Bon). Sites 2, S. Erasmo and 9, Ca' Roman are located seaward near the inlets characterized by high dynamics. The other sites are variously influenced by urban (3, Fondamente Nuove; 5, Sacca Sessola; 10, Chioggia), aquaculture (6, mussel farm) and industrial (4, S. Giorgio in Alga) inputs. The main physico-chemical characteristics of each site are listed in Table 1.

Two replicate samples of superficial sediments (0–5 cm) were collected from the 10 sites using a box-corer, kept on board in the dark and refrigerated, and rapidly transferred to the laboratory, where all analyses were performed.

2.2. Sediment analyses and S-MPP extraction

Fractions of sand $(\varnothing>63~\mu m)$ and mud $(\varnothing<63~\mu m)$ were determined on aliquots taken from one replicate by wet sieving, basically according to the method of Buchanan (1984). The wet/dry ratio was also calculated after drying sediments at 90 °C, until constant weight.

S-MPPs were extracted from each bulk sediment replicate through the density separation method of Thompson et al.

Table 1
Sampling site descriptions, sediment fractions, organic carbon (TOC) and metal pollution index (Σ As-Cd-Cr-Cu-Hg-Ni-Pb-Zn) of sediments. Analyses on trace metals and TOC in sediments had been performed in the framework of the ICSEL project; these data have been kindly provided by the Ministry of Infrastructures and Transports (Magistrato alle Acque di Venezia) through its concessionary Consorzio Venezia Nuova (partially published in Moschino et al., 2011).

Site code	Sampling site	Long E	Lat N	Description	Sand %	Mud %	TOC (%) ^b	MPI ^{a,b}
1	Palude dell Rosa	12°25′50.92″	45°30′12.88″	Freshwater	12.23	87.77	1.5	11.1
2	S. Erasmo	12°25′54.75″	45°27′37.17"	Seaward	66.53	33.47	0.5	5.2
3	Fondamente Nuove	12°20′44.27″	45°26′29.21″	Urban waste-water	46.63	53.37	0.5	8.1
4	S. Giorgio in Alga	12°16′27.11″	45°24′49.30″	Industrial discharge	12.45	87.55	1.2	16.8
5	Sacca Sessola	12°18′43.91″	45°24′10.60″	Urban traffic	31.50	68.50	1.5	11.9
6	Mussel Farm	12°18′02.02″	45°20′16.39″	Farming activities	49.33	50.67	_	_
7	Lago di Rivolta	12°13′51.00″	45°19′50.00″	Landward	19.76	80.24	1.7	8.6
8	Valle di Bon	12°12′13.51″	45°19'39.40"	Landward	19.72	80.28	1.5	9.6
9	Ca' Roman	12°17′37.92″	45°14′55.31″	Seaward	93.13	6.87	0.4	4.8
10	Chioggia	12°16′40.30″	45°13′21.00″	Urban waste-water	77.83	22.17	2.4	12.2

^a MPI = $(M_1 \times M_2 \times M_3... \times M_n)^{1/n}$ where Mn is the concentration of metal n expressed in mg kg $^{\times 1}$ of dry weight (Usero et al., 1996).

^b Data from previous studies (ICSEL).

(2004), slightly modified. An aliquot of 250 g (w.w.), taken from each sediment replicate after careful homogenization, was shaken for 1.5 min in a 2-l glass flask with concentrated NaCl saline solution (CS, 120 g l^{-1}) to reach a final volume of 1 l, and subsequently allowed to settle for 1 h. The resulting supernatant, with floating particles extracted from the sediment was filtered on a 32-um steel-wire sieve. This procedure was repeated three times consecutively. The three extracted fractions (with suspended microplastic fragments and possibly other floating lowdensity organic components) were finally pooled and resuspended in Milli-Q water, filtered through fiberglass filters (Whatman GF-F, diam. 47 mm, nominal porosity 0.7 µm), dried at 50 °C, and stored in glass Petri dishes. The same procedure was carried out without sediments, to test any ambient microplastic contamination from laboratory and equipment, which was never found. Compatible tools and clothing were always used or worn (e.g., steel tweezers, cotton laboratory coats, polymer-free gloves).

All 20 filters (2 replicated filters for each of the 10 sampled sites) were used for $\mu\text{FT-IR}$ analysis.

2.3. μ FT-IR analysis

μFT-IR analysis of S-MPPs was carried out with a Thermo Fisher Scientific (Madison, WI, USA) Nicolet™ iN10 infrared microscope equipped with an ultra-fast motorized stage and a single MCT detector. Signals were acquired in the reflectance mode, a nondestructive method which can produce IR spectra for thick, opaque materials and needs minimal sample preparation (Ojeda et al., 2009). The reflectance µFT-IR method applied here is based on surface chemical mapping, i.e., molecular mapping of microplastic fragments collected on 47-mm fiberglass filters (Harrison et al., 2012). On each filter, 12 sampling unit areas (4.5 mm² each, 5.6% of total filtered surface) were examined by µFT-IR reflectance, as the best compromise between reliability and labor (NIOSH, 1994; Ng and Obbard, 2006). The 12 areas, positioned for double-cross sampling along the surface of the filter (Fig. 2a), were selected by the automatic stage shift set by the OMNICTM PictaTM software. The spectral range was set at 4000–675 cm⁻¹, with 50-μm step size scanning (spatial resolution) at $50 \times 50 \mu m$ aperture and 8 coadded scans for each spectrum. The spectra of the resulting 12 chemical maps were collected at the spectral resolution of 8 cm⁻¹ with 8 co-scans for each spectrum, and processed with OMNICTM Picta™ to identify unknown compounds by comparing spectra with specific reference library databases (Fig. 2b, c). The spectral background was acquired on a silver-coated microscope slide. Whenever further evidence was needed, single-reflectance µFT-IR spectra were acquired with a customized aperture size according to microparticle size and shape, a spectral resolution of 4 cm⁻ and 64 co-added scans for each spectrum. When necessary (e.g., very irregular surfaces, thick or overlying particles), Attenuated Total-Reflection μ-Fourier-Transform Infrared spectroscopy (ATRμFT-IR) was also used, to confirm mapping results (Harrison et al., 2012). Instrumental parameters were selected after preliminary analyses to reach an acceptable balance among the various aspects to be taken into account when performing this kind of analysis, i.e., the suitability of the S/N (signal-to-noise) ratio, spectral and spatial resolutions, the representativeness of the examined surface, and the need to run the analyses rapidly. Results were expressed as number of S-MPPs particles per kg⁻¹ sediment d.w.

The identified particles were also observed under an optical microscope to determine their size and shape, which were categorized as fragments, fibers, films, and raw industrial pellets (Browne et al., 2010; Claessens et al., 2011).

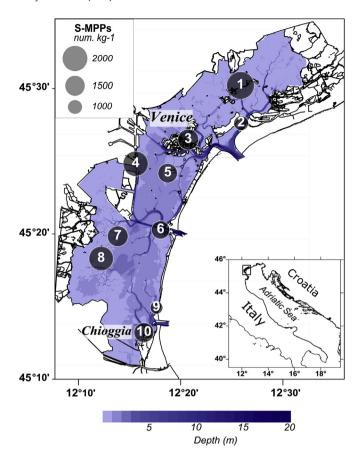


Fig. 1. Locations of sampling sites and distribution of total S-MPPs (expressed as number of particles/ kg^{-1} dry sediment).

2.4. ESEM analyses

The surface morphology of the microplastic particles was studied by environmental scanning electron microscopy-energy-dispersive spectroscopy (ESEM-EDS) (Corcoran et al., 2009). In this field of application (polymer light atoms), ESEM-EDS can be used to check the main atomic composition of polymers previously identified by μFT -IR analysis, not for semi-quantitative measurements. ESEM-EDS analyses were carried out on the filters which revealed the widest variety of polymer types, focusing on previously analyzed areas.

Analyses were performed on an FEG-ESEM QUANTA 200 F instrument (Hillsboro, OR, USA) equipped with an EDAX Genesis Energy-Dispersive X-ray Spectrometer (Mahwah, NJ, USA). A nanometric graphite layer was deposited on the surface of the filters to prevent sample charging. ESEM was operated at 25 kV electron accelerating voltage. Images were mainly obtained by secondary electrons to reach the best resolution. Observations were also performed with back-scattered electrons, which provide information on the average atomic number of the examined area. This approach discriminates heavier atoms from lighter ones like carbon (the main component in polymers) which appears darker than other heavier elements.

2.5. Data analysis

The composition of S-MPPs was studied in term of size, shape and polymer type. Results from the two replicates are expressed as mean values \pm semi-range of numbers of S-MPP kg $^{-1}$ d.w.

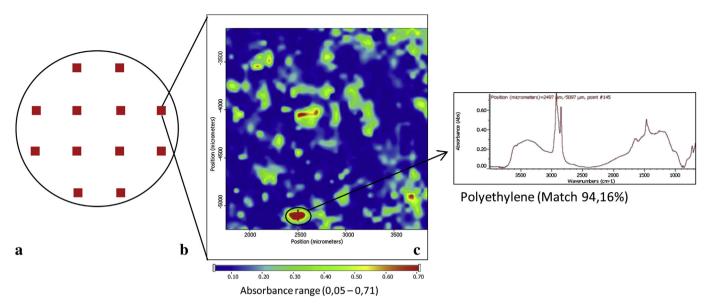


Fig. 2. Sketch of filter, with positions of 12 sub-areas analyzed by µFT-IR (a); an example of one 4.5 mm² area (b). Red spot at bottom: polyethylene fragment, see spectrum (c).

Spearman's correlation coefficients were calculated to study the statistical relationship between the amount of S-MPPs and mud fraction and the metal pollution index (MPI) to better clarify distribution patterns within the lagoon environment. In addition, by means of a data matrix composed of the polymer abundances found at each sampling site, Principal Component Analysis (PCA) was carried out, to elucidate spatial variability.

3. Results

The mud fraction ($<63~\mu m$) was very variable in the sampling sites, ranging from 7 to 88% (Table 1). As expected, this finer fraction increased from the inlets (sites 2, 9) to the inner part of the Lagoon (sites 1, 4, 7, 8). This trend matched that of previous studies on sediment grain-size distribution in the Lagoon of Venice (Molinaroli et al., 2007).

Total abundances of S-MPPs varied from 2175 to 672 kg⁻¹ d.w. (sites 1, 9), and higher concentrations were generally found in the inner parts of the Lagoon (sites 1, 4, 7, 8) (Fig. 1; Table 2). A total of ten polymer types were identified: polyethylene (PE), polypropylene (PP), poly(ethylene-propylene) (PEP), polyester (PEst), polyacrylonitrile (PAN), polystyrene (PS), alkyd resin (Alkyd), polyvinyl-chloride (PVC), polyvinyl alcohol (PVOH) and nylon (Polyamide). All samples contained at least two polymer types: PE and PP, which also accounted for more than 82% of the total S-MPPs detected in the whole sampling area (Table 3). The results of multivariate analysis (PCA) shows that factors 1 and 2 explain over 58% of total variance in

the data matrix (Fig. 3). Factor 1, explaining 38% of total variance, has high loadings of the variables PE, PVC and PVOH (0.77, 0.83 and 0.83, respectively). Factor 2 explains 20% of total variance, PS showing low loadings (-0.72). The spatial distribution of sites along Factor 2 reflects their geographical position, from seaward (Ca' Roman and Chioggia) to landward (Palude della Rosa).

Irregular fragments were observed in almost all stations (87%), whereas fibers (10%) were not detected at sites S4 and S8 (Fig. 4a). Films and pellets/granules were only occasionally identified (2% and 1%, respectively). The most frequent size (93% of observed microparticles) was in the range 30–500 μ m, longer fibers (about 2500 μ m long) being observed only rarely (Fig. 4b).

Highly significant correlations were observed between total S-MPP concentrations with the finer fraction of sediment (p < 0.01) and MPI (p < 0.05) (Fig. 5a, b).

The fragments of PE, PP and PS observed at ESEM at $500\times$, showed irregular shapes and similar surface textures (Fig. 6a–d). Instead, PEst and PAN microfibers show comparable amorphous, regular surfaces; at higher magnifications ($10,000\times$ and $15,000\times$) the surfaces appear to be weakened by adhering particles, probably indicating degradation processes (Fig. 6e–h).

4. Discussion

The approach adopted here to identify and quantify environmental microplastic particles may be considered one of the first applications of μFT -IR spectroscopy based on surface chemical

Table 2Mean \pm semi-range of the various polymer types (expressed as nr of particles kg $^{-1}$ dry sediment) detected at each sampling site within the Lagoon of Venice. PE: polyethylene; PP: polypropylene; PEPP: poly(ethylene-propylene); PEst: polyester; PAN: polyacrylonitrile; PS: polystyrene; alkyd: alkyd resin; PVC: polyvinylchloride; PVOH: polyvinyl alcohol; polyamide.

Site	PE	PP	PEPP	PEst	PS	PAN	Alkyd	PVC	PVOH	Polyamide	Total
1	924 ± 21	856 ± 405	0	158 ± 16	236 ± 24	0	0	0	0	0	2175
2	489 ± 100	245 ± 50	49 ± 49	98 ± 1	0	0	0	0	0	0	880
3	672 ± 465	570 ± 363	0	52 ± 52	104 ± 0	52 ± 52	52 ± 52	0	0	0	1501
4	1505 ± 404	202 ± 43	0	0	0	61 ± 61	0	80 ± 80	61 ± 61	0	1908
5	470 ± 174	524 ± 227	91 ± 17	107 ± 11	54 ± 54	54 ± 54	54 ± 54	0	0	0	1353
6	115 ± 115	668 ± 324	198 ± 198	99 ± 99	57 ± 57	0	99 ± 99	0	0	0	1237
7	691 ± 499	586 ± 9	99 ± 99	0	0	99 ± 99	0	0	0	0	1476
8	1136 ± 729	513 ± 98	104 ± 104	0	0	104 ± 10	0	0	0	0	1856
9	338 ± 37	241 ± 40	0	0	47 ± 47	0	0	0	0	47 ± 47	672
10	627 ± 325	509 ± 297	204 ± 98	0	0	0	0	0	0	0	1394

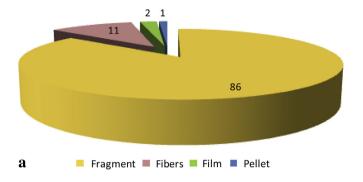
Table 3 Relative abundances (%) of the extracted polymer types and size range of the particles (in μ m).

Polymer	%	Particle size
Polyethylene	48.4	42-445
Polypropylene	34.1	15-1660
Poly(ethylene-propylene)	5.2	45-244
Polyester	3.6	15-2413
Polystyrene	3.5	42-259
Polyacrylonitrile	2.6	18-950
Alkyd resin	1.4	55-203
Polyvinylchloride	0.5	60-163
Polyvinyl alcohol	0.4	93
Polyamide	0.3	715

automatic mapping to analyze plastic particles in natural marine sediments. Only recently, Harrison et al. (2012) provided new results with this approach, highlighting the suitability of molecular mapping in detecting microplastic particles in sediment retentates. This method provides semi-automated analysis not requiring manual operations after initial settings. Its accuracy depends mainly on operator experience and ensures fast and repeatable measurements with constant instrumental parameters during the same analytical batch. This innovative aspect overcomes bias due to visual sorting and manual separation of plastic fragments, generally adopted as preliminary steps before µFT-IR (Thompson et al., 2004; Ng and Obbard, 2006; Srinivasa Reddy et al., 2006; Browne et al., 2010; Martins and Sobral, 2011). In particular, our results, although preliminary, demonstrate that the smallest fraction of particles (<1 mm) may be successfully identified by reflectance μFT-IR spectroscopy based on surface chemical mapping analysis. This fraction is known to be difficult to identify and estimate in natural matrices by classic methods relying on direct examination by optical microscope.

The recent review by Hidalgo-Ruiz et al. (2012) stresses the need to standardize plastic particle selection, emphasizing the fact that some selection criteria are only available for microplastic particles which approach the upper limit of the size range (>1 mm).

The results of this study reveal the presence of microplastic particles in all examined sediments, indicating their extensive dispersion in the Lagoon of Venice. The number of microplastics kg^{-1} d.w. sediment are higher than those found by Claessens et al. (2011) in their field survey along the Belgian coast, the only study reporting results in the same quantitative unit as ours. This may be



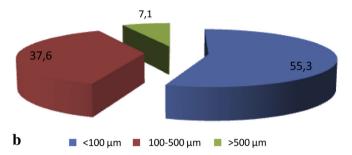


Fig. 4. Percentages of polymer shapes (a) and particle size distribution of total S-MPPs (b).

due to ambient differences and/or the different analytical methods used (i.e., visual sorting and μFT -IR in the above study; surface molecular mapping μFT -IR in ours). The spatial distribution of S-MPPs was significantly correlated with the metal pollution index, a synthetic index used to compare the total content of sediment trace metals on the whole (Usero et al., 1996). This positive correlation highlights possible links with other anthropogenic pollutants. S-MPP concentrations are higher in areas with the highest concentrations of trace metals (sites 4 and 5 near the industrial zone, and site 10 near the city center of Chioggia). These micropollutants are known to be associated with anthropogenic inputs, and they have been already considered as an indicator of overall contamination (Bernardello et al., 2006; Apitz et al., 2009). These observations suggest common contamination sources.

The direct relationship between S-MPPs and mud percentages indicates similar sinking and accumulation processes acting on

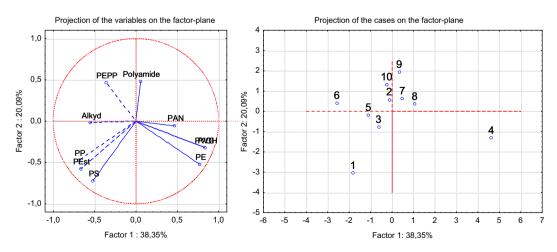


Fig. 3. Principal component analysis, based on polymer abundances evaluated at each sampling site and related site distribution. PE: polyethylene; PP: polypropylene; PEP: poly(ethylene-propylene); PEst: polyester; PAN: polyacrylonitrile; PS: polystyrene; alkyd: alkyd resin; PVC: polyvinylchloride, PVOH: polyvinyl alcohol; polyamide: nylon.

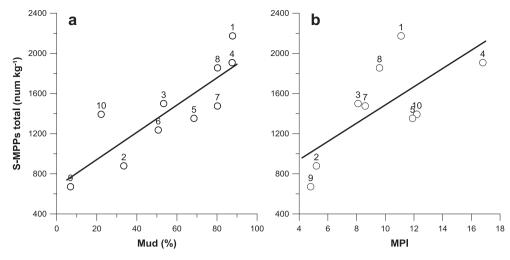


Fig. 5. (a) Correlation between total S-MPPs and mud (sediment fraction $<63 \mu m$); $R^2=0.723$, p<0.01; (b) correlation between S-MPPS and MPI, calculated as reported in Table 1; linear regression line is drawn ($R^2=0.499$, p<0.05).

both microplastics and the finer part of sediment in the Lagoon. The grain size of bottom sediments is well known to be related to water dynamics and tidal currents, decreasing from the inlets to more internal parts (Molinaroli et al., 2007) where the water residence time increases (Cucco and Umgiesser, 2006). Similarly, microplastic particles tend to accumulate in sites characterized by lower hydrodynamism (as in the inner Lagoon); the outer sites where water currents are > 1 ms⁻¹ (Gačić et al., 2002) showed the lowest concentrations. The highest concentrations of S-MPPs did turn out to be found near confined areas along the Lagoon border, which are also more influenced by freshwater inputs. Similar results were also found in another coastal area by Claessens et al. (2011), who stressed the importance of rivers as potential sources of microplastic particles to marine coastal sediments.

Our study provides initial insights into the most common polymer types found as S-MPPs in the Lagoon sediments, from which their sources may be inferred. The main fraction of microplastics consisted of irregularly shaped fragments and granules, mainly PE and PP (Fig. 6a, b), probably deriving from both land- and sea-based sources. PE was found at all sites, showing higher concentrations near the industrial zone (site 4) and in the inner parts of the Lagoon (sites 1, 8). PE is the most frequently found polymer, with a wide range of applicability. PE microfragments are known to originate mainly from packaging and breakdown of rigid plastics. PP is widely used to make rigid plastic tools, furnishings, and water and gas pipes, due to its excellent chemical and mechanical properties. PP fibers are widely used to produce textile floor coverings. carpets and rugs, and lately also sportswear; PP is also used to make fishing nets. The most common PP fiber type found in this study was 800-1000 μm in length, blue or red in color, with a typical diameter of 30-40 µm, larger than that of PEst and acrylic fibers (15-20 μm). It should be noted that geo-textile net cages filled with stones of various sizes have recently been positioned at many sites within the Lagoon, to restore intertidal marshes (Cecconi, 2005). Although little information is available on the specific composition of these nets, it is known that they are made of PE, PP and PEst, and thus probably contribute to the release of plastic fragments nearby. The highest number of PP fibers was detected at site 10 (Chioggia), which has one of the most important fishing-fleet harbors in the Adriatic. Fragments of PS are quite widespread in the Lagoon sediments in their solid form (density 1.04–1.1 g cm⁻³): PS is extensively used in packaging and for disposable items, unlike its expanded form (density 0.02–0.06 g cm⁻³), which was never found, probably due to its very low density. All plastic fragments analyzed at ESEM showed high specific surfaces due to grooving, which may indicate increased physico-chemical and mechanical degradation processes.

No PET and very few Polyamide and PVC fragments were found in our samples. PVC and PET have specific densities of 1.16—1.58 g cm⁻³ and 1.37—1.45 g cm⁻³, respectively, and thus are only occasionally isolated by CS (NaCl 120 g l⁻¹). Very few fragments of polyamide were found: this is quite surprising, due to its widespread diffusion and density (1.02—1.05 g cm⁻³), which should make it float in CS. We cannot exclude the possibility that other solutions should be adopted to make polyamide float, such as sodium polytungstate (typical density from 1.4 to 2.82—2.95 g cm⁻³, maximum reported density 3.1 g cm⁻³), as recently suggested by Hidalgo-Ruiz et al. (2012) for PVC and PET.

Despite the evidence that our approach is particularly suitable for identifying very small plastic particles ($<100 \, \mu m$), we are aware that further methodological improvements are needed for largescale applicability in environmental studies. First, it should be noted that the estuarine sediments analyzed here were particularly abundant in low-density organic components which, extracted following the density separation phase and retained on the filter surface, sometimes caused optical and spectral interferences in μFT-IR analyses. Second, reflectance μFT-IR is susceptible to refractive errors (possible spectral distortion) when very irregularly shaped plastics are analyzed (Harrison et al., 2012). It is therefore important to identify polymers in the polymer-specific IR spectral regions of absorbance, which must be free of interference, and the background signals from the filters must be as low as possible. Selecting the most appropriate membrane type would help in obtaining high-quality images with minimum spectral interference in the mid-IR region. The irregular surface of fiberglass filters (the membrane type selected to collect our samples) made it difficult to focus the entire surface of the map area during molecular map acquisition. However, signals from microplastic particles were better identified - particularly because the IR spectral range of 3200–2700 cm⁻¹, which includes aromatic CH stretching and the aliphatic CH3, CH2 and CH stretches, was almost free of intense absorption from filters. We also tested polycarbonate membranes, as suggested by Harrison et al. (2012) and cellulose ester-based filters, and both types showed flatter and more homogeneous surfaces than fiberglass filters. However, the spectral results were

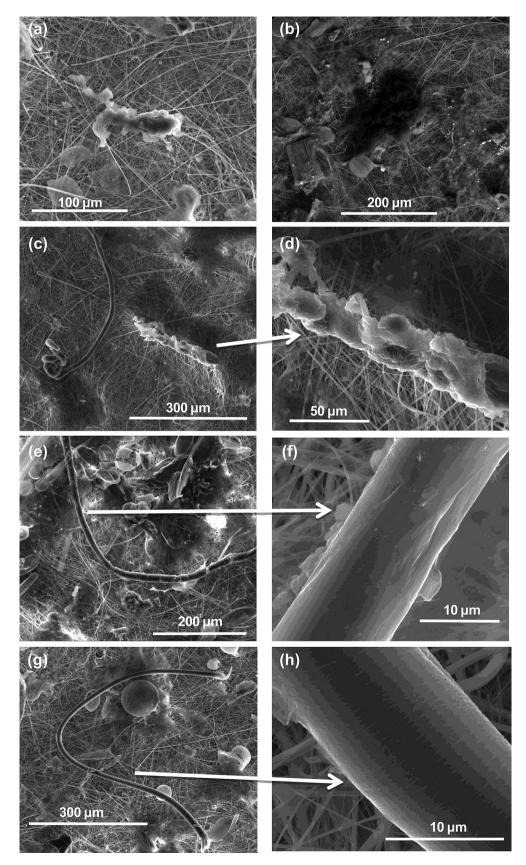


Fig. 6. Scanning electronic microscope (ESEM) images of S-MPPs. Polypropylene (a); polyethylene (b); polyester fiber (c, left) and polystyrene fragment (c, right; d); polyester fibers (e, f); polyacrylonitrile (g, h).

not so effective, mainly due to interference caused by diffuse IR absorption from their matrices.

5. Conclusions and perspectives

The analytical method applied in this study proved to be useful for initial insights into the presence of microplastics in sediments of the Lagoon of Venice, which is a very particular and complex transitional environment. Our results highlighted the widespread distribution of S-MPPs in the sediments of the whole Lagoon, providing much information on abundances and compositions. The dispersion and accumulation of S-MPPs on bottom sediments are clearly affected by local hydrodynamics in relation to their various sources. Our quantitative estimates indicate that microplastics tend to accumulate in low-dynamic areas, quite common in the inner parts of the Lagoon, showing behavior similar to that of other contaminants associated with finer sediment fractions.

Future research should be extended to assess the probable transfer of microplastic particles to local benthic filter-feeding molluscs, which are particularly exposed to the water—sediment interface. The potential transfer of microplastic particles (and associated pollutants) within the food-web should be noted, since harvesting Manila clams, *Ruditapes philippinarum*, is the primary fishery resource in the area, making the Lagoon of Venice the most important European producer, with annual production levels often approaching 40,000 metric tons over the last 15 years (Pellizzato et al., 2011)

Author contributions

A.V. performed $\mu FT\text{-IR}$ analyses, and analyzed and interpreted microplastic data. A.B. performed sediment analyses for microplastic extraction and grain-size determination, and discussed and analyzed results. P.G. provided ESEM analyses. V.M. performed sediment analyses for microplastic extraction and grain-size determination, and discussed and analyzed results. R.R. and A.S. contributed to $\mu FT\text{-IR}$ analyses. L.D.R. discussed and analyzed the results, and supervised the project. All authors collaborated on writing the manuscript, and approved the final text.

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