

Article

Macrophytes: A Temporary Sink for Microplastics in Transitional Water Systems

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Abstract: Marine macrophytes are hypothesized to be a major temporary sink for microplastics. In this study, microplastic contamination was investigated in 15 macroalgal species and one seagrass from different sites in two lagoons of the northern Adriatic Sea: the Goro lagoon and the Venice lagoon. A high percentage (94%) of the macrophyte samples contained microplastics, ranging from 0.16 to 330 items g^{-1} fw, with the prevalent size in the range 30–90 μm and an average contamination per unit of fresh weight of 14 items g^{-1} fw. Microplastic contamination displayed a site-specific, rather than a species-specific, pattern of accumulation. In addition, exopolysaccharides (EPS) displayed a significant positive correlation with the microplastics contamination on macrophytes acting as glue for the plastic particles available in the water column.

Keywords: microplastics; macroalgae; seagrasses; Nile red; EPS



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1. Introduction

In the year 2018 the world plastic production reached 359 Mt [1] and between 4.8 and 12.7 Mt of this production ends up in the ocean every year due to mismanagement and carelessness, adding to the uncontrolled plastic waste already present in the world's seas. This plastic waste has been eventually subdivided into five dimensional classes based on the size of the particles [2]: macroplastics (>200 mm), mesoplastics (200–5.01 mm); large microplastics (5–1.01 mm); small microplastics (1.00 mm–1 μm) and nanoplastics (<1 μm). The origin of microplastics can be due to a direct input of small particles in a dimensional range of 5 mm–1 μm , referred to as primary microplastics, bound to the discharge of many “open use” products, such as glitter, face scrubs, synthetic fibers from washed wears and many other goods [3]. Secondary microplastics originate instead from the macroscopic plastic litter fragmentation that occurs through interaction with atmospheric agents, waves, ultraviolet rays and biological agents [4,5]. Microplastics are an ubiquitous contaminant present in numerous environmental spheres with a contamination that expands from the highest peak on land [6] to the ocean depths [7,8], from one pole [9,10] of the globe to the other [11]. These particles are a common occurrence in seawater and all size ranges, between few microns to few millimeters, were reported in water column [12–14] and sediments [15,16] from the northern Atlantic Ocean and the Adriatic Sea.

The ingestion of microplastics in the marine environment has been reported for many organisms [17] and although debate on the toxicity and danger of these particles for marine organisms is still open [18,19], there is growing evidence that microplastics can be transferred to the food chain [20–22]. Despite this, there is still no clear evidence of microplastic magnification along the trophic chain, especially towards bigger predators [23]. Among the marine organisms investigated so far, those most susceptible to the ingestion

of microplastics are grazers and filter feeders [24,25], however knowledge regarding the contamination by microplastics of the primary producers—the feed for these organisms—is still scarce. Additionally, the macrophytes (macroalgae and seagrasses) that are the main primary producers of the transitional water systems are still largely ignored, though they are widely present in the water column and recent studies reported the accumulation of microplastics on macroalgae [26,27].

Macrophytes have been extensively used for environmental biomonitoring due to their potential as environmental indicators and as pollutant bioaccumulators [28–30]. The contaminated macrophyte tissues can be an important reservoir of contamination which can promote the transfer of microplastics to the trophic chain and increase the residence time of the contaminant in the water column.

In the present study, we analyzed 15 macroalgal species and one seagrass from two lagoons of the Northern Adriatic Sea (the Venice and the Goro lagoons) with the following aims: (i) to determine whether the macrophytes of these areas exhibit microplastic contamination, and if there is correlation between them; (ii) to evaluate differences of microplastic contamination among different species and sites aiming to understand the relative importance of the species and the sampling sites on the bioaccumulation of microplastics; and finally, (iii) to evaluate the role of macrophyte exopolysaccharides on microplastic bioaccumulation.

2. Materials and Methods

2.1. Study Area and Sampling

The Venice lagoon is the largest Italian coastal lagoon located in the northern Adriatic Sea, covering an area of 549 km² and with an average depth of 1 m. This environment is connected to the Adriatic Sea by three inlets: Lido, Malamocco, and Chioggia, from North to South, respectively. The lagoon hydrodynamic is dominated by tides, with a water volume exchanged with the sea every 12 h of about 60% [31] and an energy-decreasing gradient from seaward to landward areas from >30 cm s⁻¹ near the inlets to <6 cm s⁻¹ in more internal areas [32]. The average water residence time is 45 days, but this can reach up to 60 days in highly confined areas [33]. The main freshwater inputs are provided by two tributaries, the rivers Silone and Dese in the northwestern landward area, accounting for the 44% of the total freshwater inputs [33] and additional small inputs from the Marzenego river. In the Venice lagoon, 13 sites scattered on three hydrological basins of the lagoon within a wide range of environmental conditions were selected: Ca' Roman (CR—45°15'15.7" N 12°17'33.8" E), Cimitero (CI—45°26'35.7" N 12°21'01.3" E), Palude Maggiore (PM—45°33'17.9" N 12°30'08.8" E), Pellestrina (PE—45°18'24.8" N 12°18'16.7" E), Fisolo (FI—45°21'44.0" N 12°17'52.5" E), Fusina (FU—45°24'49.0" N 12°16'16.4" E), Lido (LI—45°24'30.4" N 12°21'43.5" E), Palude della Rosa (PR—45°30'31.9" N 12°25'25.1" E), Petta di Bo' (BO—45°16'09.9" N 12°15'01.9" E), Poveglia (PO—45°22'18.9" N 12°17'26.8" E), S. Giuliano (SG—45°27'46.2" N 12°17'22.7" E), S. Nicolò (SN—45°26'03.5" N 12°23'17.3" E) and Santa Maria del Mare (SM—45°19'29.1" N 12°18'26.8" E).

The "Sacca di Goro" lagoon is a small shallow-water embayment and is the southern lagoon of the Po' River delta system, covering an area of 26 km². It is one of the most important European sites for Manila clam farming [34]. The average depth of the lagoon is 1.5 m and it is connected to the sea by two mouths, with a water residence time between 2.5 and 122 days and an average value of 25 days [34,35]. The freshwater inflow from the "Po' di Volano" influences the western area, conversely the central area is affected by the sea inlets. The dominant winds, mainly "Bora" (from northeast) and "Scirocco" (from southeast), can significantly enhance water dynamics, increasing stream velocity up to >100 cm s⁻¹ with a concurrent reduction in water residence time [36,37]. In the Goro lagoon, four sites were selected—two along the seaward shore and another two along the landward: sea inlet (C0—44°48'13.6" N 12°18'44.7" E), seaward shore (C3—44°47'43.0" N 12°20'37.2" E), landward canal (P3—44°48'21.2" N 12°21'13.4" E) and new canal (P5—44°48'21.2" N 12°21'13.4" E).

2.2. Sampled Organisms

Ulvaceae and Gracilariaceae were among the three dominant taxa in almost all stations. The species identified included one seagrass, *Zostera marina* Linnaeus 1753, and 15 macroalgae: *Agardhiella subulata* (C. Agardh) Kraft & M.J. Wynne 1979, *Agarophyton vermiculophyllum* (Ohmi) Gurgel, J.N. Norris et Fredericq 2018, *Cladophora albida* (Nees) Kützing 1843, *Cladophora fracta* (O.F. Müller ex Vahl) Kützing 1843, *Cystoseira barbata* (Stackhouse) (C. Agardh, 1820), *Codium fragile* (Suringar) Hariot 1889, *Chaetomorpha linum* (O.F. Müller) Kützing 1845, *Gracilaria gracilis* (Stackhouse) Steentoft, L.M. Irvine & Farnham 1995, *Gracilariopsis longissima* (S.G. Gmelin) Steentoft, L.M. Irvine & Farnham 1995, *Hypnea cervicornis* J. Agardh 1851, *Laurencia obtusa* (Hudson) J.V. Lamouroux 1813, *Sargassum muticum* (Yendo) Fensholt 1955, *Undaria pinnatifida* (Harvey) Suringar 1873, *Ulva flexuosa* Wulfen 1803, and *Ulva rigida* C. Agardh 1823. The three dominant macrophyte species per biomass were collected in the sampling stations with a rake. In stations with a dominance of only one or two species, only the available specimens were collected. Macrophytes were drained of excess water by leaving them standing on the rake for 5 min and were then stored alive in decontaminated glass jars until analysis. The storage time never exceeded 24 h.

2.3. Quality Control and Assurance

Many precautions were carried out to minimize microplastic contamination during sample collection, handling and analysis: cotton lab coats and clothes were always worn in the laboratory and three procedural blanks were included in each digestion round. The blanks were considered acceptable, with less than two particles per filter, and were tested before and after the analysis of the samples. All of the solutions were filtered by GF-F fiberglass filters (0.7 µm) and all of the glassware was accurately rinsed with tap water and at least two times with filtered bidistilled Milli-Q water. The samples, collector tubes and flasks were capped with aluminum foil and glass caps during the analysis to minimize airborne contamination.

A spike recovery test was performed on the macroalgae *U. rigida* and *G. longissima*. These species were pretreated with a warm solution of sulfated polysaccharides (10 mg every 5 g of algae) extracted and purified from the same species as performed in Sfriso et al. (2017) [38] to simulate the EPS coating. A total of 200 polystyrene particles (with approximate diameter size 500 µm) were sprinkled on 10 g of algae, mixed and then split into two replicates to perform the analysis.

2.4. Macrophyte Samples Analysis

The EPS and attached microplastics were extracted in duplicate from 5 g of fresh sample in 250 mL flask by 100 mL of an extracting solution (NaCl 30 g L⁻¹, Na₂EDTA 100 mM) for 30 min in an orbital shaker at 130 RPM. The solution was collected in a second flask and the residual sample was quickly rinsed again by hand shaking two times with 50 mL of the extracting solution. The EPS analysis was carried out on 1 mL of the solution, centrifuged at 5000 RPM for 1 min for debris removal. The EPS were recovered from the supernatant by the addition of 3 mL of absolute ethanol, followed by centrifugation at 500 RPM for 10 min after overnight precipitation in the fridge at 4 °C. The EPS were measured by phenol-sulfuric acid method [39] using a glucose calibration curve for comparison and were expressed as mg per g of fresh alga (mg g fw⁻¹). For the microplastic analysis the solution was pretreated by the addition of NaOH (for a final concentration of 0.25 M) and digested at 40 °C for 24 h to remove the interference of chitin from small epibionts [25]. The solution was filtered on GF-F fiberglass filters (0.7 µm) which were rinsed with 5 mL of milli-Ro water, 5 mL of an ethanol/methanol/isopropanol (ratio 90/5/5) solution [40] and 5 mL of hexane. The number of microplastics from macrophytes was normalized on the fresh weight (fw) of the biomass and expressed as items g⁻¹ fw.

2.5. Nile Red Count

The microplastics on the filters were stained by 1 mL of Nile red solution ($10 \mu\text{g mL}^{-1}$ in hexane) in 5 cm closed Petri plates for 30 min as in Maes et al. (2017) [41] and background excess staining was removed by filtering hexane. The microplastics were identified and counted per optical field by visual recognition under a stereomicroscope equipped with a 10 W blue LED and an orange photo filter. The photos were acquired with a digital camera and processed by ImageJ to identify size (Feret diameter) in the range $30 \mu\text{m}$ – 5 mm and particle circularity (the point-by-point set of operations for image processing is described in a dedicated section of the supplementary material on image analysis).

2.6. Statistical Analysis

Non-parametric Wilcoxon tests were performed in order to assess significant differences between the concentrations of Venice and Goro stations. Furthermore, linear regression was applied to the complete dataset to study the relationship between macroalgal EPS concentrations and relative microplastic contents. Regression coefficients, relative p -value and R-squared were used to test statistical significance of the linear model. All statistical analyses were performed using R software, version 3.5.3.

3. Results

3.1. Dominant Species

The dominant species per biomass collected in every station were: C0—*G. longissima*, *U. flexuosa*; C3—*A. vermiculophyllum*, *U. rigida/laetevirens*; P3—*C. albida*, *A. vermiculophyllum*; P5—*C. fracta*, *A. vermiculophyllum*; CR—*C. linum*, *C. barbata*, *U. rigida/laetevirens*; CI—*G. longissima*, *U. rigida/laetevirens*, *A. subulata*; PM—*U. flexuosa*; PE—*C. linum*, *U. rigida/laetevirens*, *L. obtusa*; FI—*G. gracilis*, *U. rigida/laetevirens*, *Z. marina*; FU—*S. muticum*; LI—*S. muticum*, *U. rigida/laetevirens*, *U. pinnatifida*; PR—*U. rigida/laetevirens*; BO—*C. linum*, *G. gracilis*, *U. rigida/laetevirens*; PO—*C. barbata*, *U. rigida/laetevirens*, *C. fragile*; SG—*G. longissima*, *S. muticum*, *U. rigida/laetevirens*; SN—*S. muticum*, *U. rigida/laetevirens*, *U. pinnatifida*; SM—*C. linum*, and *H. cervicornis*, *U. rigida/laetevirens*.

3.2. Microplastic Recovery

The recoveries from the spike recovery test of the macroalgae *U. rigida* and *G. longissima* scored 86/100 and 90/100 particles, respectively. The blank values were always clear, except for on one occasion when two particles per filter were found.

3.3. Microplastic Size and Shape

The majority of the particles identified from the macrophytes of the Venice and Goro lagoons displayed Feret diameters within $210 \mu\text{m}$ and $120 \mu\text{m}$, accounting, respectively, for 84% and 82% of the total counts.

The highest relative abundance for the microplastics of the Venice lagoon macrophytes was in the range 30 – $60 \mu\text{m}$, the smallest size, slowly decreasing in abundance with increasing size ranges (Figure 1). Similar relative frequencies were identified in the smallest range from the macroalgae of the Goro lagoon, however the prevalent size was between 60 and $90 \mu\text{m}$, accounting for one third of the measured particles alone. This reveals a greater contribution in the range of the smallest particles from the macrophytes of the Venice lagoon.

Taking into consideration the percentage of microplastics from macrophytes in the range of 30 – $60 \mu\text{m}$ for the single stations of the Venice lagoon, four sites emerged with percentages higher than 25% corresponding to SG, SN, CR and SM. Three of these sites (SN, CR, SM) are stations near the sea inlets with very high water renewal. As for the Goro lagoon, the greatest contribution to the smallest microplastic range was due to C0, the station in front of the sea inlet.

The stations that contributed the most to the prevalent 60 – $90 \mu\text{m}$ range were C3 and P5, with more than 40% of the particles falling in this range along the canal that connects

the sea inlet with the innermost embayment of the lagoon. The circularity (0/elongated shape particles—1/circular shape particles) for the 72% of the particles was higher than 0.8, approximating the majority of the microplastics to a circular shape and only 7% displayed circularity values lower than 0.5 with elongated shapes attributable to fibers. The Venice and Goro macrophytes displayed significantly different average fiber contents (Wilcoxon test for two samples locations, $p < 0.01$) with 10% scores recorded for the Venice lagoon in comparison with the 5% fiber content found on the samples from the Goro lagoon (inset Figure 1).

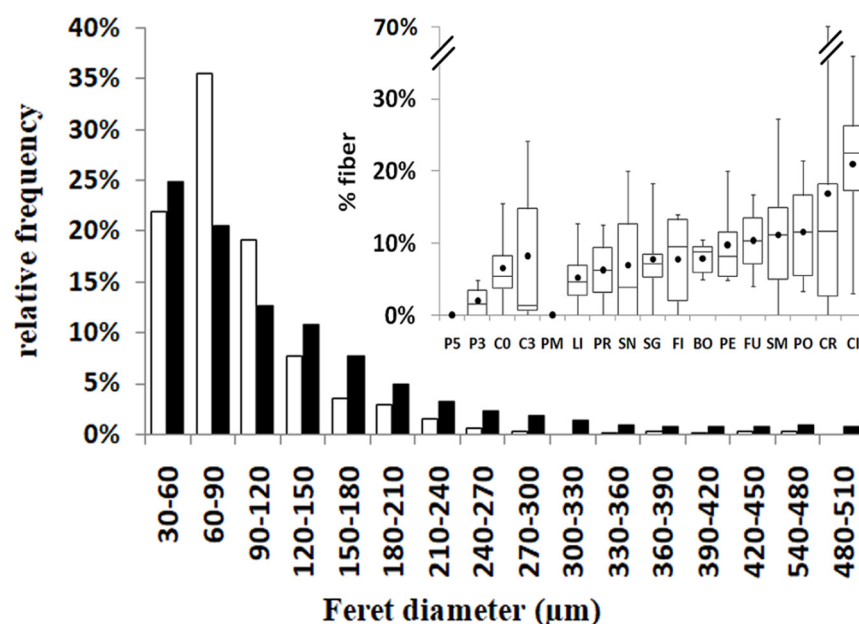


Figure 1. Histograms of the relative abundance of microplastics for size range measured by Feret diameter, from Venice lagoon (grey), Goro lagoon (white), -inset graph-Boxplot with mean (round circles) of the relative abundance of fibers in different stations from Goro (P5-C3) and Venice (PM-CI) lagoon.

3.4. Microplastic Abundance

The dominant species in the 17 sites scattered along two lagoons of the northern Adriatic Sea were investigated (a total of 41 specimens, due to the presence of three sites of the Venice lagoon -PM, PR and FU- that presented only one dominant species, while all Goro lagoon sites presented only two dominant species). The 94% of the samples analyzed contained microplastics, ranging from 0.16 to 330 items g^{-1} fw. The average microplastic content for all species and areas was 14 items g^{-1} fw, with relevant differences between different species (Figure 2). Peak values were recorded for *A. vermiculophyllum*, followed by *C. fracta*, *U. pinnatifida*, and *U. rigida*, with average values between 17 and 65 items g^{-1} fw from both lagoons. The lowest microplastic contents were found instead on *A. subulata*, *G. longissima* and *C. fragile*, within two items g^{-1} fw.

Among the characteristics of the macrophytes that most seemed to influence the surface content of the microplastics, the EPS were the most quoted candidates. The EPS contents measured on 52 samples ranged from 0.16 to 2.16 $mg g^{-1}$ fw with an average content of 0.67 $mg g^{-1}$ fw. The EPS displayed the lowest values on *C. fragile* and *G. gracilis*, with average concentrations of 0.21 and 0.29 $mg g^{-1}$ fw, conversely the highest values were identified on *U. rigida*, *U. pinnatifida* and *L. obtusa*, with average values per species of 0.85, 0.92 and 1.06 $mg g^{-1}$ fw. Eventually, a linear correlation emerged between superficial EPS content and the number of microplastics glued to the algae, as reported in Figure 3, with an approximate content of 15 particles per $mg g^{-1}$ fw of EPS. It is important to highlight that the samples from the same species with the highest EPS content in the 70% of the cases also displayed the highest content of microplastics. The relationship with EPS appears more

important than the species in determining the amount of microplastics associated with a macrophyte sample. They work like a sticky net capturing the microplastics suspended in the water column, however it is important to determine whether the microplastic content was related more to the site of origin or to the species investigated. Regarding this, the average coefficient of variation (CV) of microplastic concentration for different species within the same station (CV: 0.76) was lower than the average CV for the contamination of individual species for different stations (CV: 1.04). This seems to indicate that microplastic contamination on macrophytes was bound more to the site of origin than to the species to which it belonged, because it varied more between samples of the same species than between samples from the same station. The same behavior was also evaluated for the EPS, but the variation coefficients showed almost identical values (0.36–0.37). This leads to the conclusion that it is not only important how many EPS algae have but also the degree of contamination of the station.

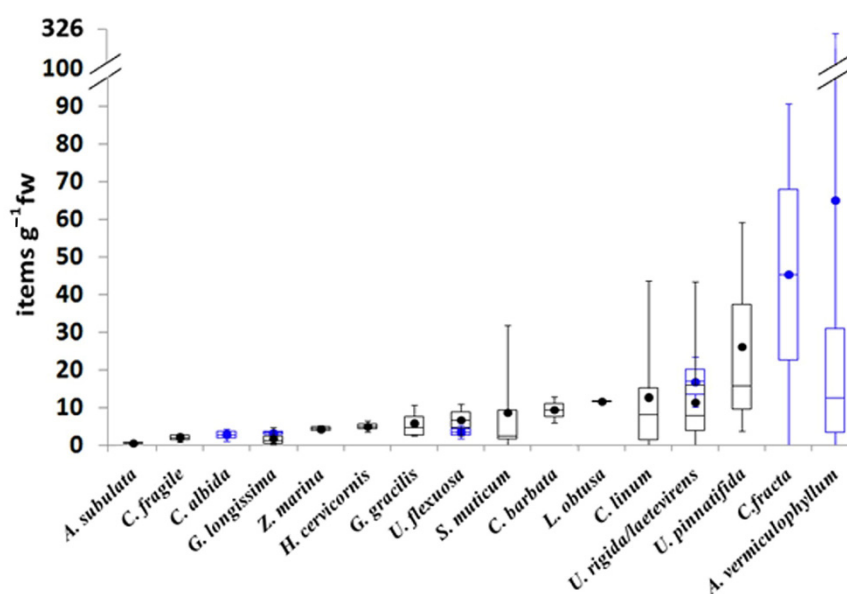


Figure 2. Boxplot with mean (round circles) of microplastic contamination in different species (combined data from all stations) from Venice lagoon (black) and Goro lagoon (blue).

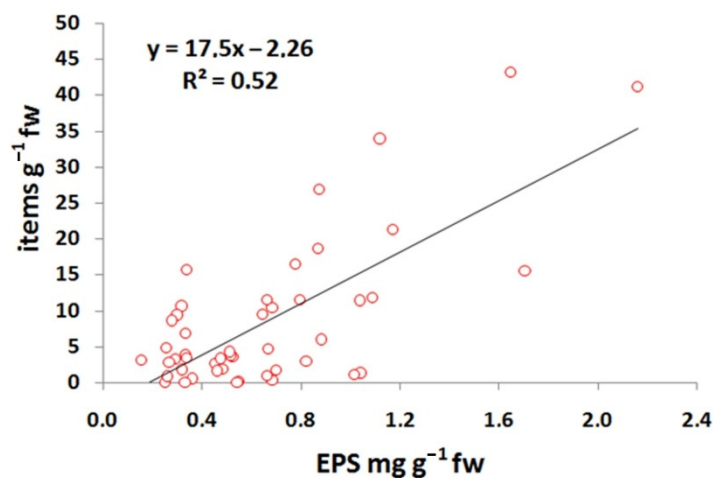


Figure 3. Plot of macrophyte EPS contents vs relative microplastic contents.

In regard to the geographical distribution of the microplastics in the Venice lagoon (Figure 4a), the stations next to the sea inlets (CR, SM, SN) displayed the lowest microplastic

contamination, except for the species from CR, which, on average, presented the second highest percentage of fibers (17%), suggesting the presence of a local contamination source probably linked to the fishing activity of nearby fisherman shelters (inset Figure 1). These areas near the sea inlets present a high tidal exchange rate and, though not very contaminated, had the highest percentage of the smallest microplastics (range 30–60 μm). Mid-level contamination in macroalgae was present in the stations midway between landward and seaward, and the highest contamination was in proximity of densely populated areas. The stations near the freshwater inputs presented only medium-low contamination, which should not justify a local freshwater supply of microplastics into the environment.

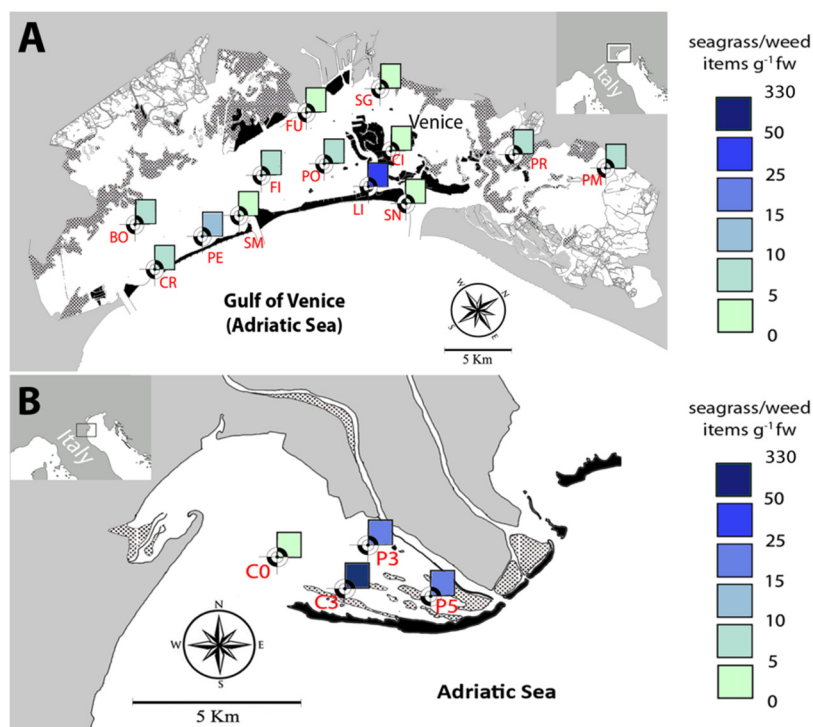


Figure 4. Postmap of the average microplastic contamination in macroalgae from the Venice Lagoon (A) and the Goro Lagoon (B).

The Goro lagoon (Figure 4b) displayed the highest microplastic scores at C3, in proximity of the seaward shore, corresponding also to the highest fiber content for the Goro Lagoon (8%). In the proximal station of P3 a high microplastic contamination was also recorded. Conversely at the station C0, in correspondence of the sea inlet, the lowest contamination was recorded, as in the Venice Lagoon. Eventually, in the most internal area of the lagoon which is subjected to freshwater inputs, macrophytes displayed a spike in concentration only in *C. fracta*, which, supposedly, may have come by drift from more contaminated areas.

4. Discussion

Microplastics are ubiquitous contaminants and have been found in most different matrices and in most remote areas, as stated in reports from terrestrial lands, freshwaters, deep ocean, mountain lakes, air, and polar regions [11,42–46]. These particles interact with living organisms and often mimic food being ingested by a long list of aquatic fauna, from small invertebrates to large predatory mammals [47]. Recent field studies on invertebrate benthic trophic chains seem to exclude biomagnification and accumulation of microplastics toward predators [25,48,49]. Conversely, the lowest levels, filter feeders and grazers, have shown the highest numbers of particles per individual. Little information is currently available on the contamination of the very base of the trophic chain, the primary producers,

the feed for grazers and filter feeders, namely micro, macro-algae and seagrasses. Some macroalgae were recently investigated along the coast of the Yellow Sea [26] in a mariculture area of the Haizhou Bay (China). The microplastic concentrations in the macroalgae of the study were, on average, very low in comparison with those found in the Venice and Goro lagoons, with concentrations ranging from 0.08 to 0.24 item g^{-1} fw and with significant variations between the stations. The low microplastic content could be attributable to the different dynamics of an open sea with respect to lagoon basins with high water residence time, such as the Venice and Goro lagoons. The values found in the Yellow Sea are, in fact, comparable with those of the algae from most marine-like stations near the sea inlets of the Adriatic Sea lagoons, characterized by pronounced hydrodynamics. Additionally, among the estimated plastic debris fluxes ($\text{kg} (\text{km day})^{-1}$) tributary to the Adriatic sea, Venice-Chioggia and Po' delta presented the highest scores [50], confirming the high degree of plastic contamination for these two areas. It has been previously suggested that microplastics might be trapped inside harbors due to their enclosed geometry and this hypothesis can be extended to large lagoon basins, such as those of the northern Adriatic Sea [51–53]. Moreover following the “boomerang effect” conceptual model proposed by Liubartseva et al. (2018) [54], the microplastic source may be local for about 50% of the polymers found.

Adherence was reported by Feng et al. (2020) [26] as the most important trapping mechanism in macroalgae, and microplastic concentrations were from 34 to 160 times higher on macroalgae than in seawater. Previous hypotheses regarding the possible role of EPS and epibiont cover on microplastic catch have been raised by Seng et al. (2020) and Gutow et al. (2016) [24,55]. Moreover the importance of EPS interaction with microplastics had already been hypothesized for the formation of aggregates in the water column by microalgae and bacteria [56,57]. Microplastic adherence was found to be directly proportional to the amount of EPS on the macrophyte surface, as identified in the correlation of Figure 3. EPS seemingly influences the capture of microplastics from seawater, more than the sample belonging to a specific taxon. This is confirmed by the fact that among macroalgae of the same species, those with a higher EPS content often also displayed a higher microplastic content. This could be because a higher EPS content virtually allows for a higher catch from sites with a lower contamination on average, and vice versa. As previously theorized by Chubarenko et al. (2016) [58], the timing of particles fouling to sink is proportional to their diameter, with smaller particles sinking faster. These present a higher rate of biofouling and are more often reported in marine sediments [53]. The mean particle half-life in the water column was reported to be between 40 and 43 days in the Adriatic Sea [50,59]. The residence times on the seaward side of the lagoons displayed values lower than 20–40 days [33,35,36], which is not enough for an efficient sedimentation of the particles that tend to escape toward the sea before settling. Moreover, the flux of microplastics in the water column has a cyclical nature which is linked to tide fluctuation, and the repeated passage of the microplastics through the macroalgal sticky net at every tide change can considerably increase the catch by macroalgae.

The sediments represent a definitive sink [60], while macrophytes are only a temporary reservoir that upon degradation at the end of their life cycle could release, in a short time, all of the bound microplastics, especially in the case of summer anoxic crises triggered by macroalgal biomass collapse, such as those produced by *Ulva* species [61]. Even excluding extraordinary events, the succession of the different species, the presence of which usually changes with the season [62] before disappearance by grazing [63] or degradation [64], leads to a cyclic release of the accumulated microplastics. The grazing pressure on lagoon macroalgae was previously estimated in *Ulva* and seagrass dominated areas in the order of 59–165% and 32–147% of the produced biomass [65], respectively. This can certainly favor the ingestion of a significant part of the attached microplastics by the grazers, as previously tested on the grazer *Littorina littorea* Linnaeus 1758 fed by Gutow et al. (2016) [24] with the microplastic contaminated macroalga *Fucus vesiculosus* Linnaeus 1753. Conversely, the release upon degradation of microplastics at the end of the algal life cycle can occur in the

form of organic particulates, such as transparent exopolymeric particles [66], which can directly settle or be ingested by filter feeders and deposit feeders [67,68], being eventually transferred to the sediments. Additionally, the 22–25% of the microplastics which have been found on macrophytes and that originate from the water column was in the 30–60 μm range, which corresponds to the size of microalgae in the optimal range for ingestion by filter feeders, larvae and bivalves [69], supporting a potential risk of contamination also for those species.

The site-specific nature of the contamination found on macrophytes and the fact that they can concentrate microplastics from the water column regardless of the species could encourage their use as biomonitors of microplastic contamination in seawater since they could integrate over time the contamination present in the water column in a specific area, as previously proposed by Feng et al. (2020) [61]. Ideal biomonitors for contaminants should be sedentary, easy to identify, abundant, long lived, available for sampling all year along, large enough to provide enough sample for analysis, tolerant to a wide range of physico-chemical parameters, and accumulators for the contaminant with a simple correlation between the tissue content and the surrounding environment [70]. Macroalgae and seagrasses seem to meet all these premises, but the last condition—the relationship between microplastic contamination in the water column integrated over time and microplastic contamination on macroalgae—has not yet been investigated. In this regard, it must be emphasized that macrophytes are already used as biomonitors for the application of the macrophyte quality index (MaQI—[30,62,71]) and if the last premise was confirmed, they could also be used for the assessment of environmental microplastic contamination.

5. Conclusions

Macrophytes are the basis of the trophic chain in transitional water systems and were found to accumulate microplastics, with 94% of the samples containing microplastics ranging from 0.16 to 330 items g^{-1} fw. The average microplastic content for all species and areas was 14 items g^{-1} fw with relevant differences between different species. Despite this, the microplastic contamination displayed a site-specific behavior and the macrophyte species were less important than the sampling sites for microplastic bioaccumulation. Additionally, the EPS coating macrophytes displayed a significant positive correlation with the microplastic contamination working as a glue and increasing the capture of the microplastics present in the water column. This study highlights how the interaction between local microplastic contamination in the water column and the abundance of EPS on the algal surface are decisive in favoring the bioaccumulation of microplastics in macrophytes. Future studies should focus on unveiling the dynamics of microplastic contamination between water, sediment and biota in order to understand the respective bioaccumulation rates in different environmental matrices.

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Abbreviations

EPS—exopolysaccharides; fw—fresh weight; MAQI—macrophyte quality index; CV—coefficient of variation. Station names: CR—Ca' Roman; CI—Cimitero; PM—Palude Maggiore; PE—Pellestrina;

FI—Fisolo; FU—Fusina; LI—Lido; PR—Palude della Rosa; BO—Petta di Bo'; PO—Poveglia, SG—S. Giuliano, SN—S. Nicolò, SM—Santa Maria del Mare; C0—sea inlet; C3—seaward shore; P3—landward canal; P5—new canal.

References

1. Plastics Europe G.M.R. The Facts 2020. In *Conversio Market & Strategy GmbH Plastics*. 2020. Available online: <https://plasticseurope.org/knowledge-hub/plastics-the-facts-2020/> (accessed on 28 October 2021).
2. Andrady, A.L. The plastic in microplastics: A review. *Mar. Pollut. Bull.* **2017**, *119*, 12–22. [[CrossRef](#)]
3. Napper, I.E.; Bakir, A.; Rowland, S.J.; Thompson, R.C. Characterisation, quantity and sorptive properties of microplastics extracted from cosmetics. *Mar. Pollut. Bull.* **2015**, *99*, 178–185. [[CrossRef](#)]
4. Artham, T.; Sudhakar, M.; Venkatesan, R.; Madhavan Nair, C.; Murty, K.V.G.K.; Doble, M. Biofouling and stability of synthetic polymers in sea water. *Int. Biodeterior. Biodegrad.* **2009**, *63*, 884–890. [[CrossRef](#)]
5. Muthukumar, T.; Aravinthan, A.; Lakshmi, K.; Venkatesan, R.; Vedaprakash, L.; Doble, M. Fouling and stability of polymers and composites in marine environment. *Int. Biodeterior. Biodegrad.* **2011**, *65*, 276–284. [[CrossRef](#)]
6. Napper, I.E.; Davies, B.F.R.; Clifford, H.; Elvin, S.; Koldewey, H.J.; Mayewski, P.A.; Miner, K.R.; Potocki, M.; Elmore, A.C.; Gajurel, A.P.; et al. Reaching New Heights in Plastic Pollution—Preliminary Findings of Microplastics on Mount Everest. *One Earth* **2020**, *3*, 621–630. [[CrossRef](#)]
7. Peng, X.; Chen, M.; Chen, S.; Dasgupta, S.; Xu, H.; Ta, K.; Du, M.; Li, J.; Guo, Z.; Bai, S. Microplastics contaminate the deepest part of the world's ocean. *Geochem. Perspect. Lett.* **2018**, *9*, 1–5. [[CrossRef](#)]
8. Abel, S.M.; Primpke, S.; Int-Veen, I.; Brandt, A.; Gerdtts, G. Systematic identification of microplastics in abyssal and hadal sediments of the Kuril Kamchatka trench. *Environ. Pollut.* **2021**, *269*, 116095. [[CrossRef](#)] [[PubMed](#)]
9. Kanhai, L.D.K.; Gårdfeldt, K.; Lyashevskaya, O.; Hassellöv, M.; Thompson, R.C.; O'Connor, I. Microplastics in sub-surface waters of the Arctic Central Basin. *Mar. Pollut. Bull.* **2018**, *130*, 8–18. [[CrossRef](#)]
10. Kanhai, L.D.K.; Johansson, C.; Frias, J.P.G.L.; Gardfeldt, K.; Thompson, R.C.; O'Connor, I. Deep sea sediments of the Arctic Central Basin: A potential sink for microplastics. *Deep Sea Res. Part I Oceanogr. Res. Pap.* **2019**, *145*, 137–142. [[CrossRef](#)]
11. Munari, C.; Infantini, V.; Scoconi, M.; Rastelli, E.; Corinaldesi, C.; Mistri, M. Microplastics in the sediments of Terra Nova Bay (Ross Sea, Antarctica). *Mar. Pollut. Bull.* **2017**, *122*, 161–165. [[CrossRef](#)]
12. Cincinelli, A.; Martellini, T.; Guerranti, C.; Scopetani, C.; Chelazzi, D.; Giarrizzo, T. A potpourri of microplastics in the sea surface and water column of the Mediterranean Sea. *TrAC Trends Anal. Chem.* **2019**, *110*, 321–326. [[CrossRef](#)]
13. Maes, T.; Van der Meulen, M.D.; Devriese, L.I.; Leslie, H.A.; Huvet, A.; Frère, L.; Robbens, J.; Vethaak, A.D. Microplastics Baseline Surveys at the Water Surface and in Sediments of the North-East Atlantic. *Front. Mar. Sci.* **2017**, *4*, 135. [[CrossRef](#)]
14. Vianello, A.; Da Ros, L.; Boldrin, A.; Marceta, T.; Moschino, V. First evaluation of floating microplastics in the Northwestern Adriatic Sea. *Environ. Sci. Pollut. Res.* **2018**, *25*, 28546–28561. [[CrossRef](#)] [[PubMed](#)]
15. Mistri, M.; Scoconi, M.; Sfriso, A.A.; Munari, C.; Curiotto, M.; Sfriso, A.; Orlando-Bonaca, M.; Lipej, L. Microplastic Contamination in Protected Areas of the Gulf of Venice. *Water Air Soil Pollut.* **2021**, *232*, 379. [[CrossRef](#)]
16. Vianello, A.; Boldrin, A.; Guerriero, P.; Moschino, V.; Rella, R.; Sturaro, A.; Da Ros, L. Microplastic particles in sediments of Lagoon of Venice, Italy: First observations on occurrence, spatial patterns and identification. *Estuar. Coast. Shelf Sci.* **2013**, *130*, 54–61. [[CrossRef](#)]
17. Bergmann, M.; Gutow, L.; Klages, M. *Marine Anthropogenic Litter*; Springer: Cham, Switzerland; Heidelberg, Germany; New York, NY, USA; Dordrecht, The Netherlands; London, UK, 2015; ISBN 1468-2311.
18. Llorca, M.; Álvarez-Muñoz, D.; Ábalos, M.; Rodríguez-Mozaz, S.; Santos, L.H.M.L.M.; León, V.M.; Campillo, J.A.; Martínez-Gómez, C.; Abad, E.; Farré, M. Microplastics in Mediterranean coastal area: Toxicity and impact for the environment and human health. *Trends Environ. Anal. Chem.* **2020**, *27*, e00090. [[CrossRef](#)]
19. Wang, F.; Wong, C.S.; Chen, D.; Lu, X.; Wang, F.; Zeng, E.Y. Interaction of toxic chemicals with microplastics: A critical review. *Water Res.* **2018**, *139*, 208–219. [[CrossRef](#)]
20. Farrell, P.; Nelson, K. Trophic level transfer of microplastic: *Mytilus edulis* (L.) to *Carcinus maenas* (L.). *Environ. Pollut.* **2013**, *177*, 1–3. [[CrossRef](#)]
21. Nelms, S.E.; Galloway, T.S.; Godley, B.J.; Jarvis, D.S.; Lindeque, P.K. Investigating microplastic trophic transfer in marine top predators. *Environ. Pollut.* **2018**, *238*, 999–1007. [[CrossRef](#)]
22. Hasegawa, T.; Nakaoka, M. Trophic transfer of microplastics from mysids to fish greatly exceeds direct ingestion from the water column. *Environ. Pollut.* **2021**, *273*, 116468. [[CrossRef](#)] [[PubMed](#)]
23. Au, S.Y.; Lee, C.M.; Weinstein, J.E.; van den Hurk, P.; Klaine, S.J. Trophic transfer of microplastics in aquatic ecosystems: Identifying critical research needs. *Integr. Environ. Assess. Manag.* **2017**, *13*, 505–509. [[CrossRef](#)] [[PubMed](#)]
24. Gutow, L.; Eckerlebe, A.; Giménez, L.; Saborowski, R. Experimental Evaluation of Seaweeds as a Vector for Microplastics into Marine Food Webs. *Environ. Sci. Technol.* **2016**, *50*, 915–923. [[CrossRef](#)]
25. Sfriso, A.A.; Tomio, Y.; Rosso, B.; Gambaro, A.; Sfriso, A.; Corami, F.; Rastelli, E.; Corinaldesi, C.; Mistri, M.; Munari, C. Microplastic accumulation in benthic invertebrates in Terra Nova Bay (Ross Sea, Antarctica). *Environ. Int.* **2020**, *137*, 105587. [[CrossRef](#)] [[PubMed](#)]

26. Feng, Z.; Zhang, T.; Wang, J.; Huang, W.; Wang, R.; Xu, J.; Fu, G.; Gao, G. Spatio-temporal features of microplastics pollution in macroalgae growing in an important mariculture area, China. *Sci. Total Environ.* **2020**, *719*, 137490. [CrossRef]
27. Li, Q.; Feng, Z.; Zhang, T.; Ma, C.; Shi, H. Microplastics in the commercial seaweed nori. *J. Hazard. Mater.* **2020**, *388*, 122060. [CrossRef]
28. Roberts, D.A.; Johnston, E.L.; Poore, A.G.B. Contamination of marine biogenic habitats and effects upon associated epifauna. *Mar. Pollut. Bull.* **2008**, *56*, 1057–1065. [CrossRef]
29. Favero, N.; Cattalini, F.; Bertaggia, D.; Albergoni, V. Metal accumulation in a biological indicator (*Ulva rigida*) from the lagoon of Venice (Italy). *Arch. Environ. Contam. Toxicol.* **1996**, *31*, 9–18. [CrossRef]
30. Sfriso, A.; Facca, C.; Ghetti, P.F. Validation of the Macrophyte Quality Index (MaQI) set up to assess the ecological status of Italian marine transitional environments. *Hydrobiologia* **2009**, *617*, 117–141. [CrossRef]
31. Masiol, M.; Facca, C.; Visin, F.; Sfriso, A.; Pavoni, B. Interannual heavy element and nutrient concentration trends in the top sediments of Venice Lagoon (Italy). *Mar. Pollut. Bull.* **2014**, *89*, 49–58. [CrossRef] [PubMed]
32. Molinaroli, E.; Guerzoni, S.; Sarretta, A.; Cucco, A.; Umgiesser, G. Links between hydrology and sedimentology in the Lagoon of Venice, Italy. *J. Mar. Syst.* **2007**, *68*, 303–317. [CrossRef]
33. Guerzoni, S.; Tagliapietra, D. *Atlante Della Laguna*; 2006 wurde von der Comune Venezia bei Marsilio Editioni; Forpress: Venezia, Italy, 2006; ISBN 88-317-8764-0.
34. Viaroli, P.; Giordani, G.; Bartoli, M.; Naldi, M.; Azzoni, R.; Nizzoli, D.; Ferrari, I.; Comenges, J.M.Z.; Bencivelli, S.; Castaldelli, G.; et al. The Sacca di Goro Lagoon and an Arm of the Po River. In *The Handbook of Environmental Chemistry, vol 5H*; Springer: Berlin/Heidelberg, Germany, 2005.
35. Shumway, S.E. *Shellfish Aquaculture and the Environment*; Sons, J.W., Ed.; Wiley: Hoboken, NJ, USA, 2011.
36. Viaroli, P.; Giordani, G.; Cattaneo, E.; Zaldívar, J.M.; Murray, C.N.; Fano, E.A.; Bencivelli, G.C.S. Sacca di Goro Lagoon—Italy In Italian Lagoon Observational Network. LaguNet. 2007. Available online: <http://www.dsa.unipr.it/lagunet/infosheet/02-goro.pdf> (accessed on 8 April 2020).
37. Meteoblue. Available online: https://www.meteoblue.com/en/weather/week/venice_italy_3164603 (accessed on 8 April 2020).
38. Sfriso, A.A.; Gallo, M.; Baldi, F. Seasonal variation and yield of sulfated polysaccharides in seaweeds from the Venice Lagoon. *Bot. Mar.* **2017**, *60*, 339–349. [CrossRef]
39. Dubois, M.; Gilles, K.A.; Hamilton, J.K.; Rebers, P.A.; Smith, F.; Dubois, M.; Gilles, K.A.; Hamilton, J.K.; Rebers, P.A.; Smith, F. Colorimetric Method for Determination of Sugars and Related Substances Colorimetric Method for Determination of Sugars and Related Substances. *Anal. Chem.* **2002**, *28*, 350–356. [CrossRef]
40. Crichton, E.M.; Noël, M.; Gies, E.A.; Ross, P.S. A novel, density-independent and FTIR-compatible approach for the rapid extraction of microplastics from aquatic sediments. *Anal. Methods* **2017**, *9*, 1419–1428. [CrossRef]
41. Maes, T.; Jessop, R.; Wellner, N.; Haupt, K.; Mayes, A.G. A rapid-screening approach to detect and quantify microplastics based on fluorescent tagging with Nile Red. *Sci. Rep.* **2017**, *7*, 1–10. [CrossRef]
42. Free, C.M.; Jensen, O.P.; Mason, S.A.; Eriksen, M.; Williamson, N.J.; Boldgiv, B. High-levels of microplastic pollution in a large, remote, mountain lake. *Mar. Pollut. Bull.* **2014**, *85*, 156–163. [CrossRef]
43. Gasperi, J.; Dris, R.; Mirande-Bret, C.; Mandin, C.; Langlois, V.; Tassin, B. First overview of microplastics in indoor and outdoor air. In Proceedings of the 15th EuCheMS International Conference on Chemistry and the Environment, Leipzig, Germany, 20–25 September 2015; pp. 1–3.
44. Horton, A.A.; Walton, A.; Spurgeon, D.J.; Lahive, E.; Svendsen, C. Microplastics in freshwater and terrestrial environments: Evaluating the current understanding to identify the knowledge gaps and future research priorities. *Sci. Total Environ.* **2017**, *586*, 127–141. [CrossRef]
45. Van Cauwenberghe, L.; Vanreusel, A.; Mees, J.; Janssen, C.R. Microplastic pollution in deep-sea sediments. *Environ. Pollut.* **2013**, *182*, 495–499. [CrossRef] [PubMed]
46. Fang, C.; Zheng, R.; Zhang, Y.; Hong, F.; Mu, J.; Chen, M.; Song, P.; Lin, L.; Lin, H.; Le, F.; et al. Microplastic contamination in benthic organisms from the Arctic and sub-Arctic regions. *Chemosphere* **2018**, *209*, 298–306. [CrossRef]
47. Wang, W.; Gao, H.; Jin, S.; Li, R.; Na, G. The ecotoxicological effects of microplastics on aquatic food web, from primary producer to human: A review. *Ecotoxicol. Environ. Saf.* **2019**, *173*, 110–117. [CrossRef]
48. Bour, A.; Avio, C.G.; Gorbi, S.; Regoli, F.; Hylland, K. Presence of microplastics in benthic and epibenthic organisms: Influence of habitat, feeding mode and trophic level. *Environ. Pollut.* **2018**, *243*, 1217–1225. [CrossRef]
49. Setälä, O.; Norkko, J.; Lehtiniemi, M. Feeding type affects microplastic ingestion in a coastal invertebrate community. *Mar. Pollut. Bull.* **2016**, *102*, 95–101. [CrossRef] [PubMed]
50. Liubartseva, S.; Coppini, G.; Lecci, R.; Creti, S. Regional approach to modeling the transport of floating plastic debris in the Adriatic Sea. *Mar. Pollut. Bull.* **2016**, *103*, 115–127. [CrossRef]
51. Claessens, M.; De Meester, S.; Van Landuyt, L.; De Clerck, K.; Janssen, C.R. Occurrence and distribution of microplastics in marine sediments along the Belgian coast. *Mar. Pollut. Bull.* **2011**, *62*, 2199–2204. [CrossRef]
52. Mathalon, A.; Hill, P. Microplastic fibers in the intertidal ecosystem surrounding Halifax Harbor, Nova Scotia. *Mar. Pollut. Bull.* **2014**, *81*, 69–79. [CrossRef] [PubMed]
53. Zhang, H. Transport of microplastics in coastal seas. *Estuar. Coast. Shelf Sci.* **2017**, *199*, 74–86. [CrossRef]

54. Liubartseva, S.; Coppini, G.; Lecci, R.; Clementi, E. Tracking plastics in the Mediterranean: 2D Lagrangian model. *Mar. Pollut. Bull.* **2018**, *129*, 151–162. [[CrossRef](#)] [[PubMed](#)]
55. Seng, N.; Lai, S.; Fong, J.; Saleh, M.F.; Cheng, C.; Cheok, Z.Y.; Todd, P.A. Early evidence of microplastics on seagrass and macroalgae. *Mar. Freshw. Res.* **2020**, *71*, 922–928. [[CrossRef](#)]
56. Lagarde, F.; Olivier, O.; Zanella, M.; Daniel, P.; Hiard, S.; Caruso, A. Microplastic interactions with freshwater microalgae: Hetero-aggregation and changes in plastic density appear strongly dependent on polymer type. *Environ. Pollut.* **2016**, *215*, 331–339. [[CrossRef](#)]
57. Summers, S.; Henry, T.; Gutierrez, T. Agglomeration of nano- and microplastic particles in seawater by autochthonous and de novo-produced sources of exopolymeric substances. *Mar. Pollut. Bull.* **2018**, *130*, 258–267. [[CrossRef](#)]
58. Chubarenko, I.; Bagaev, A.; Zobkov, M.; Esiukova, E. On some physical and dynamical properties of microplastic particles in marine environment. *Mar. Pollut. Bull.* **2016**, *108*, 105–112. [[CrossRef](#)]
59. Poulain, P.M. Adriatic sea surface circulation as derived from drifter data between 1990 and 1999. *J. Mar. Syst.* **2001**, *29*, 3–32. [[CrossRef](#)]
60. Näkki, P.; Setälä, O.; Lehtiniemi, M. Seafloor sediments as microplastic sinks in the northern Baltic Sea—Negligible upward transport of buried microplastics by bioturbation. *Environ. Pollut.* **2019**, *249*, 74–81. [[CrossRef](#)] [[PubMed](#)]
61. Feng, Z.; Zhang, T.; Shi, H.; Gao, K.; Huang, W.; Xu, J.; Wang, J.; Wang, R.; Li, J.; Gao, G. Microplastics in bloom-forming macroalgae: Distribution, characteristics and impacts. *J. Hazard. Mater.* **2020**, *397*, 122752. [[CrossRef](#)] [[PubMed](#)]
62. Sfriso, A.; Facca, C.; Bonometto, A.; Boscolo, R. Compliance of the macrophyte quality index (MaQI) with the WFD (2000/60/EC) and ecological status assessment in transitional areas: The Venice lagoon as study case. *Ecol. Indic.* **2014**, *46*, 536–547. [[CrossRef](#)]
63. Sfriso, A.; Marcomini, A. Decline of *Ulva* growth in the lagoon of Venice. *Bioresour. Technol.* **1996**, *58*, 299–307. [[CrossRef](#)]
64. Sfriso, A.; Marcomini, A.; Pavoni, B. Relationships between macroalgal biomass and nutrient concentrations in a hypertrophic area of the Venice Lagoon. *Mar. Environ. Res.* **1987**, *22*, 297–312. [[CrossRef](#)]
65. Balducci, C.; Sfriso, A.; Pavoni, B. Macrofauna impact on *Ulva rigida* C. Ag. production and relationship with environmental variables in the lagoon of Venice. *Mar. Environ. Res.* **2001**, *52*, 27–49. [[CrossRef](#)]
66. Thornton, D.C.O. Formation of transparent exopolymeric particles (TEP) from macroalgal detritus. *Mar. Ecol. Prog. Ser.* **2004**, *282*, 1–12. [[CrossRef](#)]
67. Passow, U. Transparent exopolymer particles (TEP) in aquatic environments. *Prog. Oceanogr.* **2002**, *55*, 287–333. [[CrossRef](#)]
68. Wurl, O.; Miller, L.; Vagle, S. Production and fate of transparent exopolymer particles in the ocean. *J. Geophys. Res. Ocean.* **2011**, *116*, C00H13. [[CrossRef](#)]
69. Beecham, J. *Literature Review on Particle Assimilation by Molluscs and Crustaceans*; The Centre for Environment, Fisheries and Aquaculture Science, Lowestoft Laboratory: Lowestoft, UK, 2008.
70. Storelli, M.M.; Storelli, A.; Marcotrigiano, G.O. Heavy metals in the aquatic environment of the Southern Adriatic Sea, Italy: Macroalgae, sediments and benthic species. *Environ. Int.* **2001**, *26*, 505–509. [[CrossRef](#)]
71. Sfriso, A.; Facca, C.; Ghetti, P.F. Rapid Quality Index (R-MaQI), based mainly on macrophyte associations, to assess the ecological status of Mediterranean transitional environments. *Chem. Ecol.* **2007**, *23*, 493–503. [[CrossRef](#)]