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Ecological implications beyond the ecotoxicity of plastic debris on marine phytoplankton assemblage structure and functioning☆

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ABSTRACT

Plastic pollution is a global issue posing a threat to marine biota with ecological implications on ecosystem functioning. Micro and nanoplastic impact on phytoplankton autotrophic species (e.g., cell growth inhibition, decrease in chlorophyll *a* and photosynthetic efficiency and hetero-aggregates formation) have been largely documented. However, the heterogeneity of data makes rather difficult a comparison based on size (i.e. micro vs nano). In addition, knowledge gaps on the ecological impact on phytoplankton assemblage structure and functioning are evident. A new virtual meta-analysis on cause-effect relationships of micro and nanoplastics on phytoplankton species revealed the significant effect posed by polymer type on reducing cell density for tested PVC, PS and PE plastics. Linked with autotrophic phytoplankton role in atmospheric CO_2 fixation, a potential impact of plastics on marine carbon pump is discussed. The understanding of the effects of microplastics and nanoplastics on the phytoplankton functioning is fundamental to raise awareness on the overall impact on the first level of marine food web. Interactions between micro and nanoplastics and phytoplankton assemblages have been quite documented by *in vitro* examinations; but, further studies considering natural plankton assemblages and/or large mesocosm experiments should be performed to evaluate and try predicting ecological impacts on primary producers.

1. Introduction

The massive production of plastics for a variety of uses and applications, coupled with non-adequate waste management strategies, made plastics a major environmental issue. A recent estimation stated that 10^5 tons of plastic particles are floating on oceans' surface (Eriksen et al., 2014) and the effects of these, almost widespread, pollutants on ecosystem functioning and food web is posing a threat to marine biota and they should be addressed. In particular, *in vitro* experiments demonstrated that micro and nanoplastics may have negative impacts on marine phytoplankton assemblages affecting cell growth, chlorophyll *a* content, photosynthetic efficiency and promoting colonization of microplastic substrates and hetero-aggregate formation (Sjollema et al., 2016; Long et al., 2017; Zhao et al., 2019; Zhu et al., 2019; Wang et al., 2020). These last effects are able to influence plastic debris fate by acting on buoyancy and sinking and enhancing the shift from sea surface to seafloor (Galloway et al., 2017; Kooi et al., 2017; Casabianca et al., 2020). Moreover, in a future plastic ocean, phytoplankton physiology and assemblage structure may be negatively affected with consequences on biological pump efficiency and consequently on carbon sequestration

Abbreviations: CLSM, confocal laser scanning microscopy; DA, domoic acid; DOM, dissolved organic matter; EPR, electron paramagnetic resonance; EPS, exopolysaccharides; MPs, microplastics; NMs, nanomaterials; NOM, natural organic matter; NP, nano-sized particles; PAHs, polycyclic aromatic hydrocarbon; PE, polyethylene; PECs, predicted environmental concentrations; PMMA, Poly(methyl methacrylate); POM, particulate organic matter; PP, polypropylene; PS, polystyrene; PLTX, palytoxin; PST, paralytic shellfish toxin; PVC, polyvinylchloride; TEP, transparent exopolymer particles; WWTP, Wastewater Treatment Plant.

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(Shen et al., 2020). Finally, micro and nanoplastic introduction in the marine environment, inevitably enter the food web through ingestion by the highest trophic level organisms, and consequently, can be found in seafood for human consumption with unknown health consequences (Barboza et al., 2018). In this context, interactions between micro and nanoplastics and phytoplankton assemblages may play a key role in marine ecosystem functioning with potential negative impacts on primary producers with consequences along trophic chains and ecosystem services. In order to summarize the state of art on marine phytoplankton and micro and nanoplastic relationships, a review of recently published literature was carried out. To address different aspects of these interactions, more than 100 peer-reviewed papers, published from 2009 to 2021 were selected. The search literature strategy of the present review was based on micro and nanoplastics in marine ecosystem, interaction with phytoplankton taxa, toxic effects of micro and nanoplastics on target algal species, plastic substrate colonization by marine microorganisms, hetero-aggregate formations and microplastic effects on carbon sequestration and on marine food web.

2. Sources, distribution and fate in marine environment

According to Koelmans et al. (2017) 99.8% of plastics ended in the sea since the 1950 and have degraded into micro and nanoplastics. It has been estimated that about 8 million tons of plastic waste enter the ocean each year and numbers are expected to increase (Jambeck et al., 2015). As well known, microplastics (MPs) (<5 mm), originate from fragmentation of larger plastics (Prata et al., 2019; Wang et al., 2019; Nava and Leoni, 2021) and the most common MPs polymer type are polyethylene (PE), polystyrene (PS), polypropylene (PP) and polyvinylchloride (PVC); all are found in the aquatic environment from rivers (Li et al., 2018) to the sea (Andrady, 2011; Browne et al., 2011) either floating on surface waters or on sediments (Wang et al., 2017; Casabianca et al., 2019; Choy et al., 2019). Moreover, physical, chemical and biological degradation of such mismanaged plastic products further originates nanoscale fragments named nanoplastics (<1000 μm) which rebound to their safety associated with remarkable biological, chemical and physical reactivity that allow them to interact with the cellular machinery by crossing biological barriers causing toxicity to living beings (Ter Halle et al., 2017; Corsi et al., 2020; Davranche et al., 2020; Hewitt et al., 2020; Gigault et al., 2021).

Major pathways of MPs introduction in the marine environment are river's discharge to the coast, drainage or sewage effluents (Browne et al., 2011; Lebreton et al., 2017). MPs together with larger and smaller plastic debris including nanoplastics can be transported by winds and oceanic currents for long distances up to polar regions (Obbard, 2018) and in accumulation zones such as ocean gyres (Zettler et al., 2013; Amaral-Zettler et al., 2020). Recently, the Mediterranean Sea has been identified as a great accumulation zone of plastic debris with an estimated 1000 tons surface load of plastics. Being a semi-enclosed basin characterized also by over-exploitation of coasts and densely populated, it favors plastic debris accumulation in surface waters of coastal areas (Cózar et al., 2015; Suaria et al., 2016).

In the Mediterranean Sea, current estimates of marine litter density range from 0.25 to 30 items 100 m^{-2} with macroplastics (>5 cm) largely prevailing (98%) (Macic et al., 2017; Consoli et al., 2018) and with a heterogeneous distribution along the coasts both on surface water and sediments (Alomar et al., 2016; Simon-Sánchez et al., 2019; Lambert et al., 2020). A first evidence of nanoplastic occurrence in the Mediterranean Sea revealed traces of nano-sized PS in the range of 1.08–136.7 ng L^{-1} in estuarine and surface waters of the western part of the basin with hot spots in coastal areas (Cincinelli et al., 2019; Compa et al., 2019; Schirinzi et al., 2019; Llorca et al., 2020).

However, anthropogenic MP presence has been reported in various world's oceans indicating that they are ubiquitous at the shores, as well as in the pelagic and deep-sea ecosystems. The buoyancy of both MPs and nanoplastics can be influenced by polymer density and by interactions with compounds present in the seawater. The sinking can be favored by biofilm development on the MP surface, resulting in spatial dislocation through different compartments including sea surface, deeper water column and benthic sediments (Barnes et al., 2009; Cole et al., 2011; Andrady, 2015).

Moreover, floating plastics including MPs, being a durable and persistent substratum, are subjected to the bio-adhesion of micro- and macro-organisms, favoring their dispersal from native to new habitats (Eriksen et al., 2014). .

Microbial communities, including various harmful dinoflagellate and diatom species, the so-called "plastisphere" (Zettler et al., 2013) were found to colonize plastics floating on coastal waters of the Mediterranean Sea (Masó et al., 2016; Casabianca et al., 2019). As plastics may act as a vehicle for harmful species, similarly, also biotoxins can be transported and dispersed as discussed below.

3. Impacts of microplastics on phytoplankton species

Nowadays, the environmental applications and field studies about MPs ecotoxicological effects on phytoplankton assemblages have not been directly described yet; in fact, information about this topic are highly limited, and the majority of studies focus on MPs exposure impact on marine and freshwater microalgal species by *in vitro* experiments. The interactions between MPs and phytoplankton can occur, but the potential ecological effects remain largely unknown (Wang et al., 2019). Potential effects of exposure to MPs and nanoplastics in the sub-micron range (>100 nm) to some marine phytoplankton species have been described and they included the inhibition of growth dynamics, significant reduction of chlorophyll *a* content and photosynthetic efficiency, gene expression alteration and hetero-aggregate formation (Fig. 1). Only some microalgal species are clearly affected by plastic exposure and, in order to disregard the toxicity due to other factors, only studies with physico-chemical characterization of MPs and nanoplastics were reported (Table 1). High variability in biological responses was found within phytoplanktonic species exposed to MPs and nanoplastics of different sizes and concentrations. Among marine phytoplankton species, *Skeletonema costatum* (Class Bacillariophyceae) and *Dunaliella tertiolecta* (Class Chlorophyceae) exposed respectively for 96 and 72 h to 1 μm PVC and 0.5 μm PS beads (50 and 250 mg L^{-1}) exhibited significant lower growth rate compared to controls (Sjollema et al., 2016; Zhang et al., 2017). The dinoflagellate *Karenia mikimotoi* (Class Dinophyceae) cell density also decreased upon 1 μm based size PVC exposure (24 h, 100 mg L^{-1}) (Zhao et al., 2019). The same impact was recorded in *Rhodomonas baltica* (Class Cryptophyceae), which showed significant differences in cellular growth among cultures grown with PS microbeads (10 μm, 7500 particles mL^{-1}) and control treatment after 264 h of exposure (Lyakurwa, 2017).

Conversely, in the cases of *Tetraselmis chuii* (Class Chlorodendrophyceae), *Tisochrysis lutea* (Class Coccolithophyceae), *Heterocapsa triquetra* (Class Dinophyceae) and *Chaetoceros neogracile* (Class Bacillariophyceae) no differences in cell abundance among exposed and control groups were found (range 0.004–250 mg L^{-1}, from 4 to 1872 h) (Long et al., 2017; Cunha et al., 2019).

Chlorophyll *a* content and photosynthetic rate were also analyzed in order to evaluate the effects of MPs and nanoplastics on algal productivity. In some cases, a decrease of these two parameters was observed in exposed microalgae *R. baltica*, *S. costatum* and *K. mikimotoi* at high MPs concentrations (7500 PS particles mL^{-1}, 50 mgL L^{-1}, 100 mg L^{-1}, respectively) (Lyakurwa, 2017; Zhang et al., 2017; Zhao et al., 2019). Moreover, interactions, such as adsorption of microalgae on MP surfaces can cause physical and morphological damages influencing the microalgae growth, limiting nutrients and energy transfer, leading to cell starvation and decreasing light, CO_2 and O_2 exchange (Zhang et al., 2017; Mao et al., 2018). Recently, four phytoplankton species, namely *T. pseudonana* (Class Bacillariophyceae), *S. grethae* (Class Bacillariophyceae), *Phaeodactylum tricornutum* (Class Bacillariophyceae) and

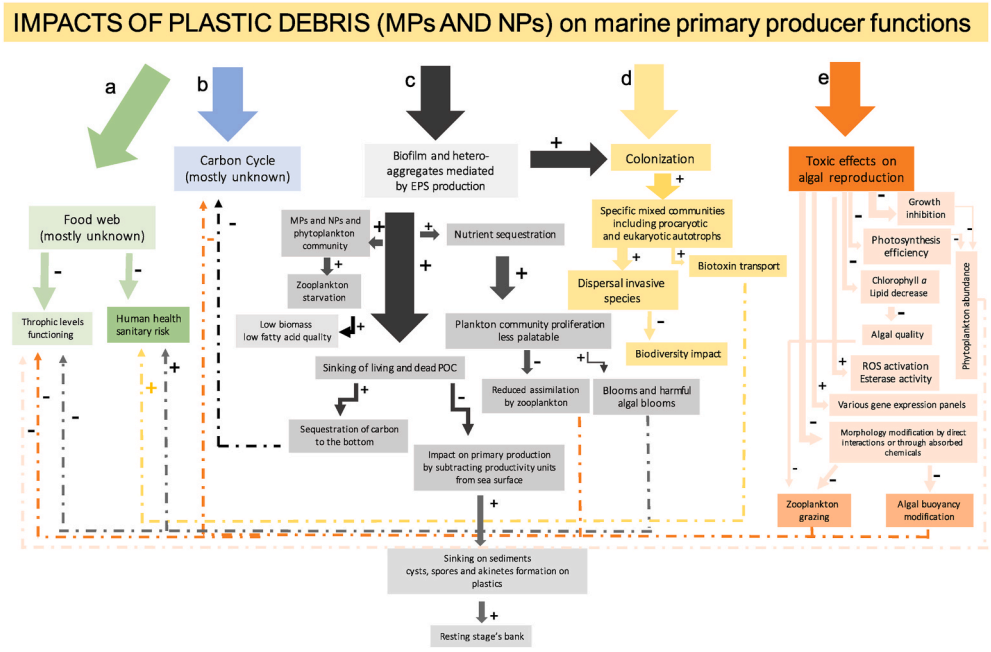

Fig. 1. Diagrammatic scheme illustrating the potential impacts of microplastics (MPs) and nanoplastics on ecological functions of phytoplankton as primary producers constituting the first level of the marine food web: a) food web, b) carbon cycle, c) aggregation, d) colonization, e) reproduction. The relative dimensions of the boxes and arrows are proportional to the importance of the compartments and the flow.

D. tertiolecta, were grown in the presence of micro- and nanoplastics and changes in cell viability, measured as relative extracted DNA amount from living phytoplankton, were observed. In particular, a decrease of species-specific viability based on lower amounts of DNA was obtained, when microalgae were exposed to PS microbeads at different concentrations (from 10^{-4} to 250 mg L^{-1}) and size (6, 1 and 0.055 μm). Results showed that cell viability declined when high concentration of larger plastic particles was used, although a stronger negative effect was found upon exposure to nanoplastics at higher concentrations (Shiu et al., 2020a). On the other hand, the majority of studies investigating adverse effects of MPs used concentrations from 2 to 7 orders of magnitude higher than those expected to be found in natural environmental scenarios (Lenz et al., 2016). In marine ecosystems, estimation of plastic debris ranged between 0.1 and 1 particle m^{-3} in the water column and from 10^3 to 10^4 particles m^{-3} on sediments (Erni-Cassola et al., 2019). Field MP concentration, estimated from manta trawl sampling (>333 μm mesh size), ranged between 0.073 and 5.33 mg L^{-1} in the South Pacific Gyre and California current system, respectively (Sussarellu et al., 2016). Moreover, it is important to consider that experimental systems, such as the use of monospecific algal cultures, are different from the real exposure scenarios, where mixed phytoplankton species coexist in assemblages with a degree of species-specific frequency, abundance and functions (i.e. carbon fixation, nutrient uptake, buoyancy). In addition to this, in natural waters, MPs are characterized by different chemical structure and at a lower concentration than those largely applied in laboratory studies using single species models (Long et al., 2017; Prata et al., 2019).

The toxic effects of MPs on phytoplankton primary producers seemed to depend on some variable features including polymer type and size, concentration, exposure time, initial cell density, cultured volume and target microalgal species (Lagarde et al., 2016; Long et al., 2017; Zhang et al., 2017; Mao et al., 2018). Thus, studies dealing with species belonging to different taxa and showing bias regarding not adequate number of trials, sample size and exposure time are difficult to be compared. By the meta-analysis of Reichelt and Gorokhova (2020), applied to a random-effect model, a weak negative response on cell growth, depending on higher plastic particles concentration, was found. Moreover, the growth inhibition was not so much due to polymer type (PS, PE and PVC) as to other factors, such as low polymer density, which seemed to have a negative effect on cell growth.

In the present review, in order to test and interpret the heterogeneity of *in vitro* experimental data on different sizes and concentration of various polymers on target phytoplankton species, a virtual meta-analysis of the published results from some papers was done using R (R; Core, 2020) environment. A series of data (Table S1) were retrieved from figures using the R package "digitize" (Poisot, 2011). For any details about the statistical analysis, see the Supplementary material section. The output of the GAM (generalized additive model), with R^2 = 0.679 capturing 68% of the total deviance, indicated that PVC and PE were characterized by a monotic effect on target phytoplankton species cell density in relation to polymer concentration. Conversely, PS was characterized by a no monotonic effect and it negatively affected cell density especially at intermediate concentration. PVC and PE, instead, always reduced cell density proportionally to their concentrations. Polymer size was not significant (data not shown). While four of the five microalgal species showed very similar responses to the different polymers; *Karenia mikimotoi* was the less sensitive species (Fig. 2).

Different experimental conditions largely influenced experimental results representing a bias in the MPs effect interpretation (Table S2). Moreover, the use of different measurement units for the growth inhibition or chlorophyll *a* content further contributed making it hard to compare results among studies. In addition, for those testing nano-scale polymeric particles, as proxy for nanoplastics (i.e. PS NPs), a full physical chemical characterization of the NP in the exposure media is lacking, then real exposure conditions effectively affecting algal cell responses are missing.

Thus, laboratory test conditions still seemed too far from mimicking a real exposure scenario. Further studies considering natural plankton assemblages and/or large mesocosm experiments should be performed with the aim of evaluating the ecological relevance of both MPs and nanoplastics/phytoplankton assemblage interaction. Similar approaches, near to real marine environmental conditions, should be applied also to phytoplankton assemblages in order to study global MPs and nanoplastics effects by evaluating indirect indicators of

Table 1
Micro and submicron plastic toxic effects on marine phytoplankton species.

Polymer type	Size (μm)	Concentration (mg L^{-1})	Microalgal species	Exposure time (h)	Sampling frequency (h)	Toxic Effects	Toxic Concentration (mg L^{-1})	Toxic exposure time (h)	Reference
PS (uncharged)	0.5	25, 250	*Dunaliella tertiolecta*	72	72	Cell density	250	72	Sjollema et al. (2016)
	6						25	72	
PS (- charged)	0.5	25, 250					250	72	
PS	10	75, 750, 7500(1)	*Rhodomonas baltica*	264	24, 48, 72, 96, 120, 144, 168, 192, 216, 240, 264	Cell density	7500	120–264	Lyakurwa (2017)
						Chl *a* content	7500	144, 216- 264	
							75, 750, 7500	240	
PVC	1	1, 5, 10, 50	*Skeletonema costatum*	96	1, 24, 48, 72, 96	Cell density	5, 10, 50	24, 48, 72, 96	Zhang et al. (2017)
							1	72, 96	
		5, 50				Chl *a* content	5	72, 96	
							50	24–96	
						Photosynthetic efficiency	5	1, 24	
							50	1, 24, 48, 72	
PE	1–5	0.5, 0.9, 2.1, 4.3, 8.3, 18.1, 41.5	*Tetraselmis chuii*	96	96	Chl *a* content	0.9, 2.1	96	Prata et al. (2018)
PE	180–212	50, 100, 150, 200, 250, 300, 350	*Dunaliella salina*	144	144	Chl *a* content	200, 250, 300, 350	144(2)	Chae et al. (2019)
PVC virgin	97–197	10, 100, 1000	*Chlorella vulgaris*	240	24, 48, 72, 96, 120, 144, 168, 192, 216, 240	Growth inhibition ratio	**10**	**96**	Fu et al. (2019)
						Biomass productivity	**10**		
PVC virgin aged(3)	93.8–183			240	24, 48, 72, 96, 120, 144, 168, 192, 216, 240	Growth inhibition ratio	**10**	**72**	
						Biomass productivity	**10**		
PS-NH_2	0.5	2.5	*Chaetoceros neogracile*	72	24, 48, 72	Esterase activity	2.5	24, 48	Seoane et al. (2019)
						Neutral lipid content	2.5	24, 48, 72	
	2	2.5				Growth rate	2.5	72	
						Esterase activity	2.5	24, 48	
						Neutral lipid content	2.5	24, 48, 72	
PVC	1	5, 25, 50, 100	*Karenia mikimotoi*	96	1, 24, 48, 72, 96	Cell density	5, 25, 50, 100	24, 48, 72	Zhao et al. (2019)
								96	
						Growth inhibitory rate	**100**	**24**	
						Chl *a* content	**100**	**48**	
						Photosynthetic efficiency	**5, 25, 50, 100**	**96**	
PE, PS and PVC	74	10, 20, 50, 100	*Skeletonema costatum*	96	24, 48, 72, 96	Cell density	10, 20, 50, 100	24, 48, 72, 96	Zhu et al. (2019)
PVC800	1					Cell density	10, 20, 50, 100	24, 48, 72, 96	
PE, PP, PET, PVC	74	200	*Phaeodactylum tricornutum*	96	24, 48, 72, 96	Cell density	200	24, 48, 72, 96	Song et al. (2020)

(*continued on next page*)

Table 1 (*continued*)

Polymer type	Size (μm)	Concentration (mg L^{-1})	Microalgal species	Exposure time (h)	Sampling frequency (h)	Toxic Effects	Toxic Concentration (mg L^{-1})	Toxic exposure time (h)	Reference
						Growth rate	200	24	
						Growth inhibitory rate	**200 (PVC)**	**96**	
						Chl *a* content	PP, PVC		
PVC	1	25, 50, 100, 200	*Phaeodactylum tricornutum*	96	1, 24, 48, 72, 96	Growth inhibitory ratio	**200**	**24**	Wang et al. (2020)
						Chl *a* content	**25**	**96**	
							200	**24–96**	
						Photosynthetic efficiency	**25, 50, 100, 200**	**24**	
			Chaetoceros gracilis			Growth inhibitory ratio	**200**	**96**	
						Chl *a* content	**200**	**96**	
						Growth Inhibitory ratio	**200**	**24**	
						Chl *a* content	**25**	**96**	
							200	**24–96**	
			Thalassiosira sp.			Photosynthetic efficiency	**25, 50, 100, 200**	**24**	

(1)Particles L^{-1}; (2) Chl *a* content increment; (3) Aged PVC. As in the considered experiments, several micro and submicron plastic concentrations were tested, the higher negative effects were reported in bold.

Fig. 2. Representation of the effects of each polymer (PVC, PE, PS) on target phytoplankton species cell density according to different polymer concentrations. The values on the Y-axes represent the standardized cell density. Only the statistically significant effects are reported.

productivity, as growth rate, abundance, species composition, carbon content, buoyancy, macromolecules composition (DNA, RNA, proteins, carbohydrates, lipids) and their ratios, photosynthetic efficiency and, therefore, ecological implications on the functioning of the phytoplankton communities in the food web (Casabianca et al., 2021).

4. Nanoplastic behaviour in seawater and toxicity on phytoplankton

The majority of the studies addressing nanoplastic impact on marine environment did not focus on their conceptual origin as the final stage of the environmental degradation of a plastic product or debris, but mainly on size, thus using polymeric nanoparticles (NP < 100 nm) as proxy for nanoplastics. On the other hand, being originated from fragmentation, those expected to reach the highest amount in the marine environment can vary substantially in size, shape and associated properties. Therefore, marine species could be exposed to a more complex fraction of plastic nano-fragments for which the impact on marine biota has been overlooked until now. The common feature between nanoplastics and nano-scale materials (NMs) is their ultimately transport behaviour, interactions with light and natural colloids, all affecting their

bioavailability and potential toxicity to marine biota (Corsi et al., 2020; Gigault et al., 2021). However, as for NMs, their detection and quantification in environmental matrices (i.e. water, soil and air) still faced major challenges due to the current analytical limitations (Jakubowicz et al., 2021). Therefore, the understanding of bio-nano interactions with marine microalgae become, thus, essential to assess their impact from single cells up to population and make predictions on cascade events at ecosystem level.

A large variety of nano-sized polymers as PS, PE, PP, PVC and Poly (methyl methacrylate) (PMMA), mainly PS nanospheres in the range 40 nm - 1 μm have been used as proxy for nanoplastics and tested at environmentally relevant concentrations and above (from μg to g L^{-1}) in short and long-term exposure conditions with several marine algal strains. Current knowledge on nanoplastic behaviour in aquatic media have been inferred from the observation of polymeric nanoparticles (NPs) (e.g., PS NPs) in controlled laboratory conditions (e.g., artificial media), at concentrations far higher than those predicted to be found in the natural environment (Corsi et al., 2020; Cai et al., 2021). Most of them were tested following available standardized ecotoxicity test protocols looking at inhibition of growth at 72 h or 96 h (e.g., ISO, 2006; OECD 201, 2011) and at sublethal endpoints (i.e., photosynthetic yield, oxidative stress) (Reichelt and Gorokhova, 2020).

As extensively discussed through the literature (Wu et al., 2019; Corsi et al., 2020), NP behaviour in high ionic strength media, such as seawater (35–40), was deeply influenced by NP surface charge. For instance, PS NPs with negative surface charge (either plain or carboxy-modified) usually form aggregates in the μm-size range in seawater, as opposed to positively charged PS NPs (as for instance amino-modified –NH_2), which generally maintain their nm-size. On the other hand, positively charged PS NPs exhibited an aggregating behaviour in the presence of dissolved organic matter (DOM), while the aggregation of their negative counterparts was not influenced by DOM (Wu et al., 2019) or seemed to be reduced (Grassi et al., 2020). However, when NOM was involved, the resulting nanoplastic behaviour was not easy to predict as it is linked to the variability and the complex interactions with NOM functional groups. As reported by Grassi et al. (2020), the concept of the biomolecular corona, defined as a layer of tightly bound proteins at the NPs surface and conceived to explain the behaviour of NPs in biological fluids (Monopoli et al., 2013), acquired different connotations when applied to complex aquatic media as natural seawater. Such so-called eco-corona is usually composed of high molecular weight biopolymers, which could be playing a more crucial role in defining the biological identity and behaviour of NPs. The ionic strength of water media, again, added further complexity: Natarajan et al., (2020), reported a gradual increase of PS NPs (from ~250 to ~500 nm) in freshwater media upon incubation with EPS for 12, 24 and 48 h. Conversely, Grassi et al. (2020) observed lower agglomeration of PS NPs (from ~850 to ~650 nm) in seawater supplied with EPS probably due to changes in NPs surface charge caused by exudates adsorption (e.g., eco-corona).

Surface charges of PS NPs have been shown to play a role in nanoplastic-microalgae interaction based on exposure time, conditions and target species. Positively charged PS NPs (PS–NH_2 50 nm EC_{50} < 1 mg L^{-1}) resulted always highly toxic showing lethal and sub-lethal effects (e.g., cell growth inhibition and density, impairment of membrane long-chain fatty acids, decrease of energy reserves, pigment content and photosynthetic yield and enhance oxidative stress, and the production of antioxidant enzymes) (Sjollema et al., 2016; Bergami et al., 2017; González-Fernández et al., 2019; Gao et al., 2021). Upon incubation in seawater or microalgae medium (>38 salinity, basic pH, and NOM), they maintained a nanoscale hydrodynamic size (<100 nm), which rebonded to their documented ecotoxicity (Della Torre et al., 2014; Bergami et al., 2016; Manfra et al., 2017; Murano et al., 2020; Pinsino et al., 2017; Marques-Santos et al., 2018; Varó et al., 2019; Wu et al., 2019).

On the contrary, carboxy-modified PS NPs (i.e., –COOH) always formed large (0.9–1.8 μm) and less harmful for marine species including microalgae, agglomerates immediately after dispersion in seawater. Recent findings, however, showed that upon prolonged incubation (38 days), size-dependent inhibition of algal growth could occur with associated increase in ROS production and photosynthesis impairment (Hazeem et al., 2020). Most notably, shifts in proteins and lipids compositions were observed, thus, leading to hypothesize that interaction at membrane level was occurring. Strong adsorption on marine microalgae of PS-COOH NPs and bare PS (range 50–100 nm and up to 50 mg L^{-1}) has been already documented upon short and long-term exposure (72 h-14 days), thus, suggesting that prolonged exposure scenarios could lead to detrimental impairments on algal cells (Bergami et al., 2017; Sendra et al., 2019; Bellingeri et al., 2020). In particular, the formation of shorter chains (2 cells instead of 4 or 8 ones) in *S. marinoi* suggested potential ecological implications for their buoyancy (Bellingeri et al., 2020). Taking into consideration that nanoplastics originating from fragmentation and/or weathering in the marine environment are expected to bear negatively charges due to surface oxidation and acquisition of functionalities (e.g., carbonyl groups) (Gigault et al., 2016; Andrady, 2017; Lehner et al., 2019), these bio-interactions may be relevant in terms of ecological cascade impact on phytoplankton assemblages. More recent studies conducted using environmental nanoplastics obtained from weathered PE MPs collected from the North Atlantic gyre showed more harmful effects of weathered compared to virgin ones by blocking cell division of the marine diatom *T. weissiflogii* (48 h, 1–10,000 μg L^{-1}) (Baudrimont et al., 2020).

As also reviewed in Corsi et al. (2021), nanoplastic surface properties (e.g., surface charge, functional groups, degree of weathering) play an important role in defining their affinity for biological membranes, together with environmental interactions occurring in seawater, including adsorption of existing pollutants or biological molecules (i.e., EPS as mentioned above). These are important drivers of ecotoxicity and they can significantly affect nanoplastic behavior and biological effects on phytoplankton assemblages. More studies should focus on understanding such processes starting from adhesion dynamics and temporal changes towards chemical and biological entities including colonization by microbial assemblages of the larger nanoplastics close to 1 μm.

Even if the range of reported effect concentrations nanoplastics is wide (EC_{50} from 0.1 mg L^{-1} to 100 mg L^{-1}) (Sjollema et al., 2016; Bergami et al., 2017; Zhang et al., 2017; Bellingeri et al., 2020), according to the previously reported factors influencing toxicity, the values are far above PECs for the marine environment (1 pg L^{-1} – 20 μg L^{-1}) (Lenz et al., 2016). However, data regarding the environmental occurrence and distribution of nanoplastics are still limited and regions characterized by high levels of plastic pollution, as coastal marine areas in the Mediterranean Sea, could exceed PECs and approach toxicity thresholds.

5. Bio and chemical adhesion and colonization of plastic substrates

In the marine ecosystems, biological interactions between MPs and biota are documented including biofouling, their presence inside fecal pellets, ingestion and transfer through the food web (Clark et al., 2016). In particular, microorganisms are able to colonize the surface of floating MPs, which represent a robust and durable substratum for bio-adhesion (Fig. 1). The accumulation of microorganisms on submerged plastic surfaces is a phenomenon known as biofouling that starts from the adsorption of organic molecules and it follows by the increased adhesion of bacteria, diatoms and other microorganism communities. Finally, these microorganisms are linked together in a biofilm by extracellular polymeric substances (Flemming and Wingender, 2010). This biofilm is formed within hours upon release into the marine environment and it increases in density and structural complexity within days. Further, within weeks, algal fouling communities occur colonizing the plastic surfaces (Donlan, 2002; Lobelle et al., 2011; Zettler et al., 2013).

Moreover, the plastic hydrophobic surfaces allow a more rapid colonization by microorganisms than the hydrophilic surfaces, and, in this way, the formation of microbial biofilms may affect the physical characteristics of plastics and MPs favoring their sinking through the water column (Long et al., 2015; Galloway et al., 2017; Casabianca et al., 2020). Plastic sinking can start within 2 weeks depending on plastic particle size, type, shape, roughness and environmental conditions (Fazey et al., 2016). Furthermore, plastic surface hydrophobicity and buoyancy are affected by biofilm formation and consequently, microorganism colonization and accumulation influenced the downward movement of MPs to the sea bottom and lead to an increased sinking rate (Kaiser et al., 2017; Kooi et al., 2017; Song et al., 2018). These interactions between bacteria, microalgae, protozoans, fungi and MPs generated biofilms composed by phylogenetically and functionally complex communities, also collectively known as plastisphere, microbial assemblage, biofouling or periphyton (Zettler et al., 2013; Rummel et al., 2017). These microbial assemblages took advantage of a biofilm as competition and survival strategies, accumulation of nutrients, and protection against environmental stress and predation (e.g., dehydration and ultraviolet radiation) (Donlan, 2002). Recently, confocal laser scanning microscopy (CLSM) allowed differentiating and counting bacteria, archaea and unicellular eukaryotes responsible for biofilm formation in PE, PP and PS plastic debris. Diatoms were the first colonizers being the most abundant taxa at the early stages of biofilm formation (after 1 week). However, they became less abundant with time being replaced by other microbes, probably because of diatom grazing copepod trigger. A time-dependent increase in microbes' abundance, both photosynthetic and non-photosynthetic, on all substrates at the end of incubation was documented (Zhao et al., 2021). Similar results were obtained for plastic items collected from the North Pacific Gyre. SEM revealed that bacteria and pennate diatoms were the most abundant, and they were found in association with coccoid bacteria, other centric diatoms, dinoflagellates, coccolithophores and radiolarians; diatom abundance increased on plastic debris with rough surfaces in sites with the highest plastic concentrations (Carson et al., 2013). Recently, by taxon-specific qPCR assay, diatom and dinoflagellate assemblages were found in plastics from coastal waters and off-shore of the Mediterranean Sea. Harmful microalgae were found; in particular, potentially toxic diatom *Pseudo-nitzschia* spp., both planktonic and benthic toxic dinoflagellate *Alexandrium pacificum, A. minutum* and *Ostreopsis* cf. *ovata,* respectively, were found on floating plastic at different concentrations. The most abundant was *Pseudo-nitzschia* spp. with the 74% of presence and 6.6 10^3 cells cm^{-2} per plastic item, followed by *A. pacificum* (38%) and by *A. minutum* and *O.* cf. *ovata* (21%) with maximum abundance of 73 and 259 cells cm^{-2}, respectively. Other toxic dinoflagellates, such as *Lingulodinium polyedrum, Protoceratium reticulatum* and *Gonyaulax spinifera,* were found in scarce or low amounts. The phytoplankton species adhesion to plastic surfaces was also confirmed by experimental adhesion rate, and *A. pacificum* resulted to adhere the most rapidly followed by *S. marinoi* and *P. multistriata*. Very low adhesion was found for *L. polyedrum* (Casabianca et al., 2019). The potential different ability to colonize, and thus, to adhere to the various plastic substrates may be explained by chemical-physical interactions that arise between substrate debris and microorganism walls or membranes up to external surfaces of living organisms (Zettler et al., 2013). In a recent study of Casabianca et al. (2020), based on electron paramagnetic resonance (EPR) spectra of selected spin probes able to enter the phytoplankton cell interface and interact with the plastic surface, the interactions between diatom *S. marinoi* and dinoflagellate *L. polyedrum* and plastic surfaces was characterized. The specific siloxane groups on *S. marinoi* silica frustule were found to be involved in the binding with the hydrophobic plastic surface of PE. On the contrary, the external cellulosic thecal plates of *L. polyedrum* poorly adhere to the plastic surface and cells seemed to roll on the plastic substrate also due to cellular spherical shape.

Recently, the advent of next-generation DNA sequencing techniques provided the characterization of microbial assemblages both colonizing plastic debris and living in surrounding water in oceanic gyres. Generally, the plastisphere communities, investigated by distribution analyses of Operational Taxonomic Units (OTUs), were genetically distinct from those in the water column. In addition, biogeographical differences were found based on ocean basin scale comparison of plastisphere community composition: Pacific and Atlantic plastisphere communities were different (Amaral-Zettler et al., 2015; Bryant et al., 2016). All these findings have important implications in the study of microbial interactions with plastics, because biofouling communities may have specific properties of adhesion mediated by chemical-physical composition and site-specific effects at different locations.

Therefore, the colonization of marine floating MPs by harmful and/or toxic microorganisms, including phytoplankton species, is evident as these new substrates may represent a vehicle for allochthonous species dispersal and their introduction in new habitats (Masó et al., 2016; Casabianca et al., 2019; Nava and Leoni, 2021). Moreover, if toxins producing species are present within the plastisphere community, biotoxin transport by MPs can represent a potential threat. It has been estimated that domoic acid (DA), palytoxin (PLTX) and paralytic shellfish toxin (PST) compounds can be potentially transported at various amounts ranging from 5 to 443 ng cm^{-2}, from 1 to 62 ng cm^{-2} and from 1 to 72 pg cm^{-2}, respectively (Casabianca et al., 2019). At the end, there may be a potential human sanitary risk through ingestion of contaminated seafood. Indirect toxin accumulation on plastics and consequently plastic/biotoxin uptake by filtering feeding animals or by transfer throughout trophic level organisms may be a plausible scenario.

Moreover, based on the calculated total plastic marine debris distribution, Zhao et al. (2021) estimated that from 2.1 10^{21} to 3.4 10^{21} microbial cells, of both photosynthetic and non-photosynthetic functional microorganisms, populate plastic debris globally. This large quantity of cells carried by plastic debris may potentially impact biodiversity due to epi-plastic floating community dispersal by plastics transport (Casabianca et al., 2019; Cunha et al., 2019).

Moreover, dense potentially harmful microorganisms' monolayers on plastic surfaces may have a ballasting effect leading to a downward transport caused by a reduced buoyancy of floating particles, as discussed below (Lobelle and Cunliffe, 2011; Cózar et al., 2014). Several studies have reported the ability of micro- and nanoplastics to interact with inorganic and organic contaminants through surface adsorption which is driven by specific plastic properties, as type of polymer, size, shape and aging as well as those of the receiving aquatic media (i.e., osmolarity, pH, NOM) (Wang et al., 2020; Huang et al., 2020; Mei et al., 2020; Reichel et al., 2021). The adsorption process is made through hydrophobic and/or steric interactions and, in some cases, even to covalent bonds. This process in which the high surface area to volume ratio of the μm and sub-μm plastics and the presence of functional charged groups seemed to play a significant role and it followed a non-linear sorption isotherms (Koelmans et al., 2015; Town and Van Leeuwen, 2020). Emerging pollutants including pharmaceuticals have been documented to adsorb on both micro- and nanoplastics through electrostatic and hydrophobic interactions and hydrogen bounding (Lee et al., 2019; Velzeboer et al., 2014; Wang et al., 2020; Wu et al., 2016). PS NPs adsorption properties and kinetics have been largely tested as proxy for nanoplastics and their role in affecting bioavailability, uptake and toxicity of adsorbed pollutants; even their trophic transfer have been demonstrated on a case by case study according to particles properties and those of the aquatic receiving media. Therefore, nanoplastics, more than larger counterparts, can deliver environmental pollutants through a *Trojan horse* mechanism being their nano-scale properties associated to stronger adsorption and their nano size to an easier uptake and translocation among organs and tissues (Town and Van Leeuwen, 2020).

In freshwater model species, co-exposures of micro- and nanoplastics with aquatic pollutants (i.e. PAHs) resulted in either a different biodistribution or increased bioaccumulation of the co-pollutant, thus, further proving the hypothesis of *Trojan horse* mechanism (Chen et al.,

2017; Trevisan et al., 2019, 2020). In marine environment, a recent study by Davranche et al. (2019) showed a significant sorption of lead (Pb) to real nanoplastics obtained from the fragmentation of MPs collected from the North Atlantic gyre, thus, supporting the role of size, but, also of aging of plastic on the adsorption process. A further confirmation is provided by the study of Mao et al. (2020) in which aged PS NPs adsorbed more heavy metals than pristine, probably as a consequence of an increase in surface hydrophilicity, as already hypothesized by other authors (Liu et al., 2019, 2020). Regarding the role of the ionic strength of the aquatic media, less adsorption was observed in seawater compared to freshwater, thus, supporting the hypothesis that dissolved ions can affect the interplay between nanoplastics and inorganic contaminants in seawaters (Cortés-Arriagada, 2021). Furthermore, the recent evidences obtained in a freshwater system that nanoplastics are transferred through the food chain by their adhesion on algal cells (PS NPs, 50–60 nm) and end up into the gut of the fish affecting lipid metabolism, causing histopathological damages in liver and ultimately their behavior, are increasing the concern associated to their role as carrier of toxic chemicals (Cedervall et al., 2012; Chae et al., 2018). Adsorption properties of the nanoplastics can not only significantly affect the fate of toxic chemicals in aquatic ecosystems, but also their uptake, accumulation and distribution in organs and tissues where they wouldn't normally be accumulated. This may cause new biodistribution and bioaccumulation scenarios and associated eco-toxicity, which need to be further investigated, in particular, in marine food chains where information is still scarce or almost absent. Taking into consideration that larger amount of nanoplastics originating from fragmentation of MP debris is expected to be present in marine surface waters and in coastal areas where higher amount of both legacy and emerging pollutants are released from human activities (i.e., soil run-off, sewages from wastewater treatment plants, WWTPS, and industrial activities), the knowledge of bio interaction occurring with the phytoplankton assemblages could be extremely relevant for predicting risk scenarios across several levels of biological organization. Furthermore, the current lack of eco-toxicity data obtained by using environmental nanoplastics makes such predictions even more urgent, and further studies should be carried out by using them as reference material.

6. Plastic EPS hetero-aggregate formation and sinking

Marine microalgae, as well as other organisms, such as bacteria, cyanobacteria, fungi and yeasts produce exudates as EPS, which are mainly constituted of long-chain polysaccharides: macromolecules belonging to the carbohydrate group, proteins and DNA (Flemming and Wingender, 2010). EPS are species-specific viscous gel-like structures with sticky properties that can aggregate into larger particles when organic or mineral compounds are present (Bhaskar et al., 2005; Galgani et al., 2019). The production of EPS by microorganisms is responsible for important processes, such as marine organic aggregate formation, microbial colonization, and pollutant mobility. EPS are known to be precursors of marine snow and microgels and, if the exuded polysaccharides attract organic particles and bacteria, the formation of these aggregates is very likely resulting in higher sinking velocities and downward fluxes of carbon material to the bottom (Berman-Frank et al., 2007).

EPSs have been widely shown to interact with environmental pollutants, such as metals and organic molecules and, ultimately, also plastic and NMs (Koukal et al., 2007; Quigg et al., 2013; González-Fernández et al., 2019). Given the fundamental role played by EPS in ocean ecology and the biogeochemical cycle of carbon, it is important to investigate the occurrence and consequences of the interactions between pollutants, EPS, and phytoplankton assemblages (Fig. 1). The exposure of phytoplankton to PS MPs and NPs have been shown to increase the protein-to-carbohydrate ratio (P/C) of excreted EPS leading to the production of a matrix with increased stickiness (Shiu et al., 2020a). Depending on physico-chemical conditions (i.e. pH, temperature, UV light) and DOM (dissolved organic matter) composition, DOM can organize in aggregates >0.7 μm to form particulate organic matter (POM) (Decho and Gutierrez, 2017). Since DOM polymers are amphiphilic, their assemblage into microgels and consequent formation of POM is believed to be driven by both hydrophobic interactions and Ca^{2+} bridging. The hydrophobic domains, mainly owned by proteins, are those involved in the interactions with the plastic surface.

The affinity of EPS for the plastic surface is probably also involved in the documented adhesion of nanoplastics to phytoplankton cells (Bergami et al., 2017; Zhang et al., 2017; Bellingeri et al., 2019). In the study of Bellingeri et al. (2020) on the effects of PS NPs on diatom *S. marinoi*, it was observed by TEM that the adhesion of PS NPs to the algal surface was driven by an algal biopolymer matrix. Even if the reported adhesion caused no acute effects for microalgal growth up to 50 μg mL^{-1} exposure, a net reduction in microalgal chain length was observed and it was attributed to the adhesion of PS NPs to the fultoportula processes (FPP), the silica structures responsible for the linking of cells to each other.

The assembly of microgels from EPS excreted by various phytoplankton species is induced and accelerated by PS NPs. This was shown to have a positive correlation to the protein content of EPS and brought to the formation of bigger aggregates compared to the absence of NPs (Chen et al., 2011; Shiu et al., 2020b) (Fig. 3). In this context, an alteration of the DOM-POM transition process could take place together with the incorporation of nanoplastics inside biogenic aggregates, with possible implications for the vertical transport in the water column of both nanoplastic and organic aggregates.

Both micro- and nanoplastics entering marine ecosystems may incorporate into marine organic aggregates composed by biopolymers and phytoplankton giving rise to hetero-aggregates (Michels et al., 2018; Cunha et al., 2019). Nanoplastics and microplastics were incorporated within biogenic aggregates in laboratory generated marine snow and this showed to mutually alter the behaviour of both plastics and marine snow. Depending on the relative density of incorporated MPs, marine snow was observed to sink slower or faster than their counterparts with no MPs, promoting also the transport of low-density MPs to the benthic environment (Long et al., 2015; Porter et al., 2018). Some studies also demonstrated that this process greatly increased the ingestion of micro and nanoplastics by benthic filter feeders causing the uptake of MPs up until 300 times more compared to the exposure to MPs in a marine snow-free medium (Ward and Kach, 2009; Porter et al., 2018).

In particular, the study of Cunha et al. (2019), demonstrated how two marine microalgae *Tetraselmis* sp. (Class Chlorodendrophyceae) and *Gloeocapsa* sp. (Class Cyanobacteria), known to be EPS producing species, when exposed to PMMA and PS micro-sized particles (<106 μm and 106–250 μm, respectively) showed the ability to form EPS-plastic hetero-aggregates when exposed to both plastic types. These EPS producing capacities proved to have species affinities, and a species-specific correlation between EPS production and MP aggregate formation was found. In particular, *Gloeocapsa* sp. resulted in the most EPS and aggregate productive species. These results highlighted the potential of microalgae to secrete EPS and flocculate MPs favouring their vertical mobility and deposition (Cunha et al., 2019).

Recently, mesocosm experiments have been performed to understand if MPs presence could influence microbial activity by increasing the production of organic carbon and aggregates sinking. Autotrophic and heterotrophic microorganisms grew with higher production of TEP (transparent exopolymer particles) in presence of PS microbeads (30 μm). The study showed that these gel-like polysaccharide aggregates can combine with organic compounds and MPs, originating larger aggregates able to sink to the bottom (Galgani et al., 2019).

In a future scenario of a continuous release and/or formation of plastic debris, this mechanism may have consequences on MPs and nanoplastics fate at sea and, as discussed below, may have implications on carbon and other organic material downward export (Galgani and Loiselle, 2021).

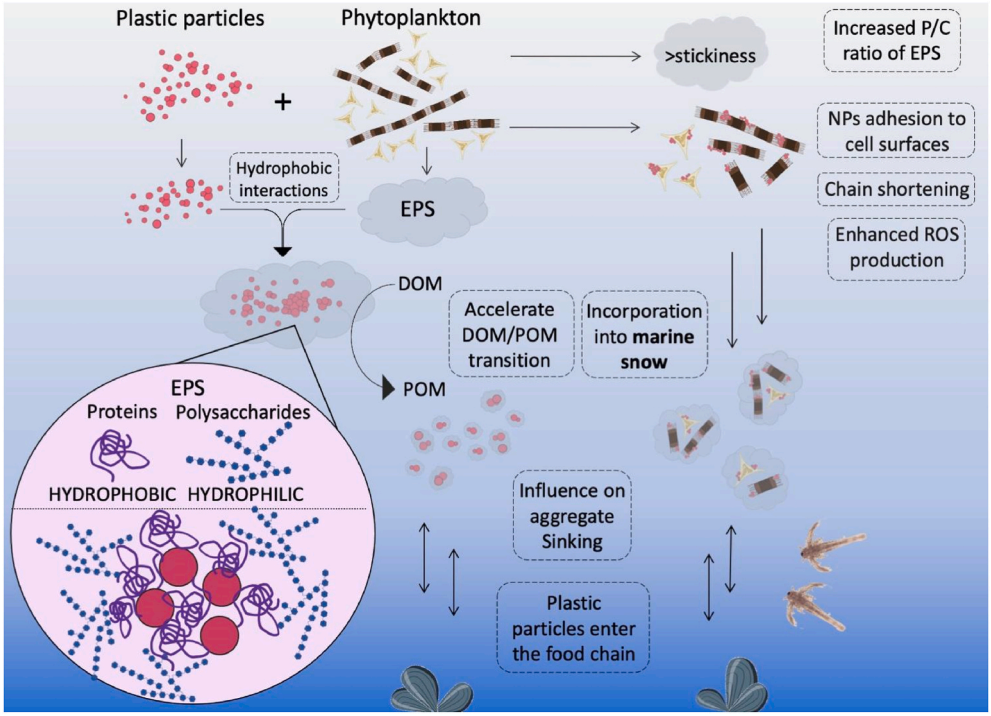

Fig. 3. Schematic illustration of micro and nano plastic interaction with phytoplankton and EPS and resulting effects on their mutual fate.

7. Effects on carbon sequestration by microplastics

Autotrophic phytoplankton species as primary producers are one of the key basal players of the biological carbon pump, which is the main process responsible for the vertical distribution of carbon in the oceans (Passow and Carlson, 2012). Phytoplankton is able to fix about 50 Gt carbon per year (Bach et al., 2016). The biogeochemical process starts from the atmospheric CO_2 fixation by autotrophic phytoplankton assemblage, in the euphotic zone, to produce particulate organic carbon (such as carbohydrates, lipids and proteins) through photosynthesis to be transferred, after microbe and zooplankton processing, in the form of fecal pellets and organic aggregates to sediments where it is sequestered for centuries (Hader et al., 2014; Turner, 2015; Hulse et al., 2017). The biological pump efficiency depends on phytoplankton physiology and assemblage structure, which in turn depend on physical and chemical conditions of the marine ecosystem. Due to the globally increasing flux of plastic debris from land to the sea, it is expected that the estimated amount, currently ranging between 4.8 and 12.7 million metric tons, will increase by an order of magnitude in the next few years (Jambeck et al., 2015). In such a scenario, the association between phytoplankton assemblages and MPs and nanoplastics may reduce the chance of phytoplankton contacting with light irradiance and negatively affecting photosynthesis activity (Fig. 1). This could be due to a shading effect caused by marine floating MPs responsible for an irradiance decrease. Indeed, the shading effect hypothesis was not confirmed by *in vitro* experiments as only a negligible influence on diatom *S. costatum* photosynthesis was found (Zhang et al., 2017). A reasonable explanation is that, under laboratory conditions, high light irradiance is provided and, even if white-colored MPs in the exposed condition partially blocked the light, the remaining was enough allowing microalgae growth and photosynthesis that was not different from the control (not exposed) condition. This optimal situation is far from marine environment conditions where light is a limiting factor for primary producers and where a continuous increasing input of different MPs, from color to size and polymer type are present (Jambeck et al., 2015; Long et al., 2015). Thus, the interaction between MPs and phytoplankton could alter functional aspects of these primary producers, such as the chlorophyll *a* concentration, photosynthesis, growth rate, colony size and morphology (Yokota et al., 2017). As discussed above, phytoplankton growth and photosynthesis efficiency were negatively affected by exposure to MPs, even if different results, not always in agreement, regarding this aspect were obtained. In particular, the major effects were observed when high plastic concentrations were tested (from 50 to 250 mg L^{-1}) (Sjollema et al., 2016; Long et al., 2017; Zhang et al., 2017; Seoane et al., 2019; Zhao et al., 2019). Moreover, MPs can adsorb on their surface substances from the water column, as nutrients, organic matter and hazardous hydrophobic contaminants. Assimilation of nutrient compounds by plastic materials may alter their concentration availability both decreasing in surrounding oligotrophic waters, but also increasing within plastic environment with potentially negative or positive effects on phytoplankton growth rates inside or outside plastic colonized community (Galloway et al., 2017; Nolte et al., 2017; Chen et al., 2020). In nutrient depleted conditions, small phytoplankton species can be favored causing a lowered storage of particulate organic matter (POM) sinking by biological pump and altering the dynamic of phytoplankton assemblage structure and function (Hutchins and Fu, 2017). On the other hand, the presence of floating plastics useful as grown substrates, may enhance marine phytoplankton species proliferation and, as plastic pollution is destined to increase, in a future compromised environment, microalgal blooms could be more frequent with negative impact on humans' health and ecosystem services. As discussed in the next section, this negative impact could be amplified by the toxic effect of MPs exerted on zooplankton, which no longer feeds on phytoplankton as a first choice of food (Zhang et al., 2020) (Fig. 1).

Thus, if field phytoplankton growth and photosynthetic efficiency are negatively impacted by actual and future MPs dispersal in marine environment, changes in primary producers' community could occur with negative impacts on marine carbon pump. A reduction in air-sea CO_2/O_2 exchange and carbon sequestration by reduced phytoplankton assemblages can be expected (Shen et al., 2020).

Moreover, the presence of MP debris may induce a higher production of EPS, which favor the formation of hetero-aggregates trapping various microorganisms, among them phytoplankton assemblages. Phytoplankton, which will be less abundant, production rate will therefore be

modified in the water column. This could potentially lead to a decrease of carbon export by subtracting phytoplankton assemblages with negative effects on ocean productivity. A shutdown of the biological pump would lead to a significant accumulation of inorganic carbon in the surface linked to a high increase of atmospheric CO_2 concentrations (Maier-Reimer et al., 1996).

An assessment of carbon biomass based on cell volume measurements and carbon per cell content for various microbial taxa was performed on biofilm covering plastic material placed in seawater. Authors estimated that plastic-associated carbon biomass ranged from 1.5×10^3 to 1.1×10^4 metric tons. Meanwhile, this represented an extra introduction of carbon biomass, which could alter marine areas characterized by oligotrophic waters, such as subtropical gyres known as plastic accumulation areas. In a future scenario of increasing plastic input, this large microbial biomass quantity carried by plastic debris could potentially affect biodiversity, autochthonous ecological functions, and biogeochemical cycles within the oceans (Zhao et al., 2021).

From this overview, in an increasing levels of plastic pollution scenario it is likely that MPs may affect the marine microbial cycling of carbon with unpredictable impacts on global ocean productivity (Galgani et al., 2019; Galgani and Loiselle, 2021).

8. Microplastic effects on food web

The interaction of microorganisms with plastics are responsible for surface biofilm formation and biofouling processes due to microbial colonization of floating MPs surfaces. It can increase the ingestion, and consequently, the trophic transfer of MPs through aquatic consumers (Rummel et al., 2017). Due to the huge amount of small plastic debris (micro and nanoplastics) in marine environments, the MP interactions and ingestion by zooplankton can occur impacting on the primary consumer's ecological role in marine ecosystems and food chain (Cole et al., 2013). It has been found that primary consumers may preferentially ingest particles covered by biofilms as they feel them more palatable carrying higher nutritional quality than plastics not covered by a microbial biofilm or just only by phytoplankton (Rummel et al., 2017; Vroom et al., 2017). Ingested MPs by zooplankton may cause a false satiety, which derived by the co-ingestion of inert plastic together with regular food; consequently, a decrease of feeding activity with negative effects on phytoplankton representing POC grazing can occur (Cole et al., 2013; Wright et al., 2013). If the zooplankton community, known to be important phytoplankton consumers and involved in carbon sequestration processes, reduce the consumption of POC sequestered by phytoplankton, ecological implications in oceanic carbon cycle can be expected. In fact, the lack of top-down regulation by zooplankton grazing could lead to a phytoplankton abundance increase with potential occurrence also of harmful algal blooms (Cole et al., 2015; Foley et al., 2018) (Fig. 1).

Furthermore, the food quality for zooplankton is essentially related to chemical composition of phytoplankton taxa. Recently, it has been noticed that the diatom *C. neogracile* exposed to 2.5 mg L^{-1} PS (PS–NH_2) of 0.5 and 2 μm size showed a significant decrease in the neutral lipid content. In particular, after 72 h, the lipid content of diatom cells exposed to MPs was 50% less than the control. The reduction was probably operated by this diatom species to counteract the stress conditions of plastic debris exposure negatively influencing cell growth and photosynthesis. This control mechanism could have ecological implications on the food quality, because the negative effect on lipid metabolism may reduce the nutritional quality of microalgae with adverse impacts on food chain functioning affecting the process from primary to higher level consumers (Seoane et al., 2019). In fact, the changed diet of zooplankton leads it to starvation due to less ingested phytoplankton or to low quality and content of lipids, contributing to negative effects on zooplankton development and reproduction (Kong and Koelmans, 2019).

The MP biofouling is able to decrease plastic buoyancy leading to plastic particles density increase, and this modification can induce MPs to sink towards seabed (Andrady, 2011). MPs could also be downward transported as zooplankton fecal pellet forms even with slower sinking velocity (Wieczorek et al., 2019; Shore et al., 2021). Once MPs reach marine sediments, particles may be toxic or harmful for benthic fauna communities by reducing their abundance or representing a potential ecological risk, because plastics become bioavailable and a consequent trophic transfer throughout marine food web may occur (Van Cauwenberghe and Janssen, 2014; Green, 2016). The ingestion of MPs was done by passive mechanism of filter feeding organisms (Ryan, 2019), or by many marine fauna, including zooplankton, mistaking them for food (Cózar et al., 2014; Wright et al., 2013). In addition to these negative impacts, the presence of MPs in high trophic levels of seafood (i.e. shellfish and fish) causes concern about the related sanitary risk and the potential effects of these pollutants for human health (Barboza et al., 2018).

Thus, it would be important to understand the potential effects of MPs on lower trophic levels organisms because MPs may undergo biomagnification with potential implications for higher level organisms (Prata et al., 2019).

9. Gaps and recommendations

Plastic debris pollution has become a widespread problem affecting the marine environment with potential heavy ecological implications. Consequences of potential interactions between plastic polymers and phytoplankton assemblages are still overlooked. Without filling this gap, it would be difficult to understand what can happen at community level and to predict ecological impacts of micro and submicron plastics on phytoplankton assemblage structure and functioning. Thus, suggestions and recommendations for future research are proposed.

In particular, smallest plastic debris occurrence and distribution along the marine water column and on bottom sediments still present some challenges to be addressed, thus, adequate reliable methods and analytical tools to be applied in monitoring programs are required. Moreover, size and shape, polymer composition and aging of plastic items retrieved along water column and inside marine organisms need to be further investigate to predict bio/ecological impacts of micro and nanoplastics.

Based on the available literature and our studies, a full physical-chemical characterization of micro and nanoplastic properties, which include size, surface charges, colonization and eco-corona formation in ecotoxicity testing is mandatory (i.e. exposure media with and without testing organisms). Concerning nanoplastics, it would be fundamental to investigate also sub-lethal effects as more likely predictors of potential ecological implications, in order to come closer to the possibility of predicting negative outcomes to populations and ecosystems. To achieve this aim, more chronic exposure studies using also environmental nanoplastics should be conducted and focus on long-term exposure scenarios. This will allow both to increase the chances of observing possible negative outcomes and support mitigation and/or restoration measures.

More environmentally relevant concentrations need to be tested, based on the amount of MPs and nanoplastics found at sea and PEC values in order to compare effect-concentrations obtained in the past studies mostly performed with high exposure levels. In addition to this, the most widespread and representative polymers retrieved in marine environments should be used, fully characterized and applied in *in vitro* experiments.

In order to define the plastic adsorption properties towards biological and chemical compounds including microorganisms, various phytoplankton species should be tested, both in single and mixed cultured experiments, using also mesocosms to investigate the interactions between MPs and/or nanoplastics and primary producers. This could be useful for predicting cascade events along trophic chain as phytoplankton assemblages represent a base transfer component to the

trophic web. Further, to try to figure out consequences on phytoplankton assemblages' ecological role, micro and nanoplastic interaction with primary producers should be investigated also in field studies and performing ecological endpoints in ecotoxicity studies, as for instance buoyancy of phytoplankton assemblages, carbon budget exported downward sediments or incorporated into microplastic and plastic debris on floating surface.

Finally, standardization of methods used both in *in vitro* and in field experiments, needs to be carried out and new derived guidelines should be shared by the scientific community to avoid future bias in experimental set up.

10. Conclusions

As discussed throughout this review, the main issue is represented by the ecological implications on marine phytoplankton assemblage functioning. In particular, the highest concerns are: i) the potential reduced phytoplankton contact with light due to plastic debris shading effect which can reduce photosynthesis activity; ii) the interactions between micro and nanoplastics and phytoplankton can alter functional aspects of primary producers, as photosynthesis, growth rate, colony size and morphology; iii) hetero-aggregates and colonization of plastics can alter POC metabolism, zooplankton grazing, noxious and alien species dispersal, and harmful algal blooms; iv) the negative impact of plastic pollution on phytoplankton assemblage function can have negative impacts on carbon sequestration and carbon pump; v) human sanitary risks can emerge through the alteration of the enhanced productivity and plastic dispersal of potentially toxic phytoplankton.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.118101.

Author statement

Silvia Casabianca: Conceptualization, Investigation, Writing – original draft, Writing – review & editing. Arianna Bellingeri: Writing – original draft, Writing – review & editing. Samuela Capellacci: Writing – review & editing. Alice Sbrana: Methodology. Tommaso Russo: Methodology. Ilaria Corsi: Conceptualization, Writing – original draft, Writing – review & editing. Antonella Penna: Conceptualization, Writing – original draft, Writing – review & editing. All authors have read and agreed to the published version of the manuscript.

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