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Effects of nanomaterials on marine invertebrates

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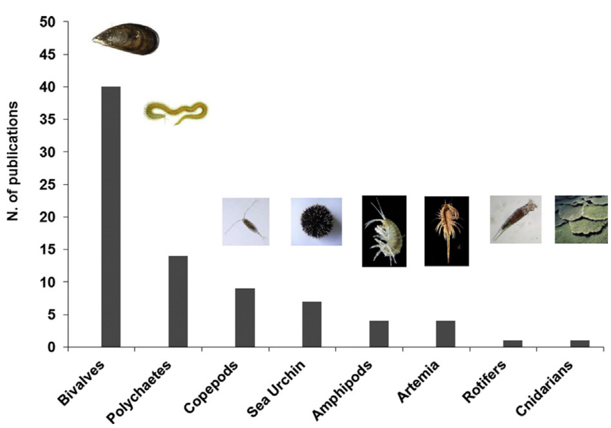
HIGHLIGHTS

- Marine invertebrates are significant targets for NPs released in the environment.
- Most data on bivalves and echinoderms, much less in sediment dwelling species
- Main biological responses: immunomodulation, oxidative stress, embryotoxicity
- NP interactions with environmental/biological components affect their fate/toxicity.
- More information on eco/bio-interactions of NPs in the marine environment is needed

GRAPHICAL ABSTRACT



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ABSTRACT

The development of nanotechnology will inevitably lead to the release of consistent amounts of nanomaterials (NMs) and nanoparticles (NPs) into marine ecosystems. Ecotoxicological studies have been carried out to identify potential biological targets of NPs, and suitable models for predicting their impact on the health of the marine environment. Recent studies in invertebrates mainly focused on NP accumulation and sub-lethal effects, rather than acute toxicity. Among marine invertebrates, bivalves represent by large the most studied group, with polychaetes and echinoderms also emerging as significant targets of NPs. However, major scientific gaps still need to be filled. In this work, factors affecting the fate of NPs in the marine environment, and their consequent uptake/accumulation/toxicity in marine invertebrates will be summarized. The results show that in different model species, NP accumulation mainly occurs in digestive tract and gills. Data on sub-lethal effects and modes of action of different types of NPs (mainly metal oxides and metal based NPs) in marine invertebrates will be reviewed, in particular on immune function, oxidative stress and embryo development. Moreover, the possibility that such effects may be influenced by NP interactions with biomolecules in both external and internal environment will be introduced. In natural environmental media, NP interactions with polysaccharides, proteins and colloids may affect their agglomeration/aggregation and consequent bioavailability. Moreover, once within the organism, NPs are known to interact with plasma proteins, forming a protein corona that can affect particle uptake and toxicity in target cells in a physiological environment. These interactions, leading to the formation of eco-bio-coronas, may be crucial in determining particle behavior and effects also in marine biota. In order to classify NPs into groups and predict the implications of their release into the marine environment, information on their intrinsic properties is clearly insufficient, and a deeper understanding of NP eco/bio-interactions is required.

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1. Introduction

Recent environmental fate models underline that nanowastes will end up in the aquatic environment, thus potentially affecting natural ecosystems and human health (Bystrzejewska-Piotrowska et al., 2009; Brar et al., 2010; Liu et al., 2014). Marine ecosystems, historically seen as a major sink of anthropogenic contaminants, will receive consistent amounts of nanomaterials (NMs) and nanoparticles (NPs), whose intrinsic and extrinsic complexity are making the prediction and assessment of their fate, exposure and biological effects a major challenge (Klaine et al., 2008). As recently discussed in our overview on fate models and tools (analytical and biological) for ecosafety assessment and design of NMs entering the marine environment (Corsi et al., 2014), still major scientific gaps need to be filled. The development for instance of quantitative approaches for integrating more realistic NP exposure scenarios and predicting ecosystem impacts are urgently needed for a proper risk assessment (Gottschalk et al., 2013). Ecotoxicological studies on marine organisms have so far reported a wide variety of biological injuries in species belonging to different trophic levels, from planktonic to benthic species, including fish; these studies had the general aim to identify potential biological targets as well as suitable models for both risk assessment and prediction of marine environmental implications (Minetto et al., 2014; Baker et al., 2014; Matranga and Corsi, 2012). In order to achieve this goal, basic information on the factors affecting the behavior of NPs released in the marine environment, and consequent uptake/accumulation/toxicity by representative species must be taken into account. The importance of evaluating the potential impact of NP exposure on aquatic invertebrates has been underlined (Baun et al., 2008; Canesi et al., 2012; Baker et al., 2014; Corsi et al., 2014; Matranga and Corsi, 2012; Canesi et al., 2015; Rocha et al., 2015). The first studies were mainly carried out in freshwater species utilizing standard ecotoxicity tests, with less than 20% of published papers on marine species (Cattaneo et al., 2009). However, the number of publications on NP ecotoxicity in invertebrates has exponentially grown in the last few years, with a strong contribution of those investigating NP accumulation, sub-lethal effects and mechanisms of action, rather than on acute toxicity. Among these, the percentage of studies on marine species has risen considerably (up to 38% of the total) (Fig. 1A). Bivalve molluscs are so far the most studied marine invertebrate group (50%), whereas less attention has been focused on sediment-dwelling invertebrates (benthic infauna) (about 20%) (Fig. 1B).

Mytilus spp. represent the most utilized bivalve model: special emphasis has been given to the effects of different types of NPs on the immune system and on the main tissues involved in NP uptake and accumulation, *i.e.* the gills and the hepatopancreas (reviewed in Canesi et al., 2012, 2015; Rocha et al., 2015). Scattered information is available on other bivalve species and marine invertebrate groups (echinoderms, annelids). In this work, those aspects related to the effects of NPs on immune function, oxidative stress and early development in different invertebrate species will be analyzed in more detail. Moreover, the concept that such effects may be influenced by NP interactions with biomolecules both in the external environment and within the body fluids, forming eco-bio-coronas, will be introduced.

2. Behavior of different particles in SW

Environmental implications of NPs are strongly linked to their peculiar features such as particle surface charge, size, shape, functionalization and coating, all properties that affect their interaction with the surrounding media and the resulting fate and toxicity (Klaine et al., 2008). For instance, dispersion and aggregation or agglomeration in aqueous solutions are driven not only by NP size and surface charges, but also by several parameters of the receiving media, such as pH, ionic strength (osmolarity) and presence of natural organic matter (NOM) (Corsi et al., 2014; Keller et al., 2010; Petosa et al., 2010). Natural environmental scenarios are currently barely represented in nanoecotoxicological studies, this being mainly due to substantial lack of information on interactions between different NP types and exposure media such as for example natural sea water (NSW) *vs* artificial sea water (ASW). The high ionic strength that also affects pH, as well as organic matter content, has been reported to play a significant role on NP aggregation, thus affecting their fate in the water column and sediments (Chen et al., 2011). In our recent work with marine mussels *Mytilus galloprovincialis*, co-exposure to titanium dioxide NPs (n-TiO_2) and $CdCl_2$ in ASW resulted in reduced Cd toxicity and increased Ti accumulation in selected tissues (*i.e.* gills) (Della Torre et al., 2015). On the other hand, such an effect was not observed in the digestive gland, suggesting that interactions with biomolecules may affect the fate and effects of NPs within the organism. Bioavailability, as well as biodistribution and consequent biological responses, are highly dependent on exposure mechanisms, but also on the interactions of NPs inside the body of the organism itself. Further studies on NP behavior within the aquatic environment, as well as into the internal environment of exposed organisms, are therefore strongly needed.

Both heteroaggregation and homoaggregation are driven by NP surface charges and the chemical composition of the surrounding media, due to the presence of elevated concentrations of inorganic ions as well as organic molecules such as polysaccharides, proteins and colloids (Praetorius et al., 2014; Zhou et al., 2013). Moreover, the presence of functional groups on the surface of NPs, more than their core composition (metal-based, carbon-based, *etc.*) is now being considered to play a major role in sorption to biofilms in high ionic strength media such as NSW. Single NPs may barely adsorb NOM, while "bridging effects" due to colloids interacting with multiple particles can increase aggregation. For instance, colloidal polymers produced by algae known as exopolymeric substances (EPS) can influence aggregation

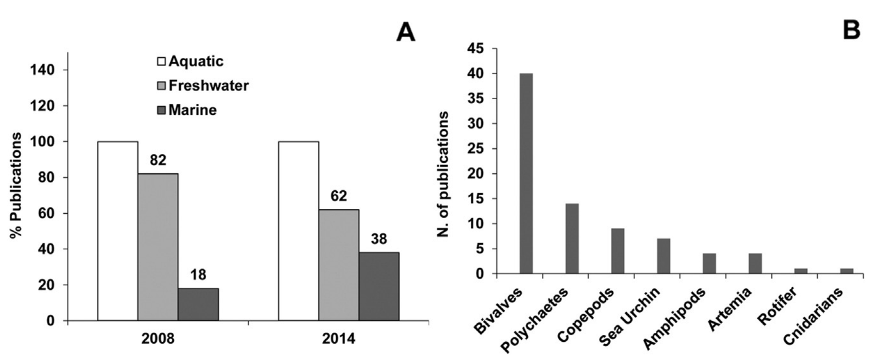

Fig. 1. Studies on the effects of NPs on aquatic invertebrates. A) Percentage of publications on freshwater and marine invertebrates with respect to total publications on aquatic invertebrates at 31/12/2008 and 31/12/2014 (source http://www.ncbi.nlm.nih.gov/pubmed); B) Number of publications on different marine invertebrate groups and genera at 31/12/2014.

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