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Manufactured nanoparticles in the aquatic environment-biochemical responses on freshwater organisms: A critical overview

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ABSTRACT

The enormous investments in nanotechnology have led to an exponential increase of new manufactured nano-enabled materials whose impact in the aquatic systems is still largely unknown. Ecotoxicity and nanosafety studies mostly resulted in contradictory results and generally failed to clearly identify biological patterns that could be related specifically to nanotoxicity. Generation of reactive oxygen species (ROS) is one of the most discussed nanotoxicity mechanism in literature. ROS can induce oxidative stress (OS), resulting in cyto- and genotoxicity. The ROS overproduction can trigger the induction of anti-oxidant enzymes such as catalase (CAT), superoxide dismutase (SOD) and glutathione peroxidases (GPx), which are used as biomarkers of response. A critical overview of the biochemical responses induced by the presence of NPs on freshwater organisms is performed with a strong interest on indicators of ROS and general stress. A special focus will be given to the NPs transformations, including aggregation, and dissolution, in the exposure media and the produced biochemical endpoints.

Contents

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1. Introduction

Nanotechnology has emerged as a fast growing sector impacting key economical fields and providing new engineered nano-enabled products, constituted by nanoparticles (NPs), with novel and unique functions that reach the market every day (Bour et al., 2015). NPs are defined as materials with a size between 1 and 100 nm on at least one dimension, having unique physicochemical properties differing from their bulk forms due to their greater surface area to volume ratio. This size related-properties results in larger reactivity and higher mobility (Rauscher et al., 2014), leading to numerous applications in medical diagnostics, electronics, computers, cosmetics and environmental remediation. The worldwide consumption of NPs is expected to grow from 225,060 metric tons in 2014 to nearly 584,984 metric tons in 2019 representing an annual growth rate of 21.1% (Research, 2015). Although impressive, these numbers are in fact "expected" values obtained by estimation or modeling. The lack of legislation for nanotechnologies gives the manufacturers no onus to reveal the real figures, thus, indeed, these predicted values are most probably significantly higher. The absence of real numbers hinders the prediction of the NPs amount that are actually being released into the environment (Piccinno et al., 2012). Even though several studies have been performed with the goal of modeling NPs environmental concentrations (Gottschalk et al., 2013), they should only be considered as guidelines, since they derive from uncertain data about the NPs production (often obtained by surveys to the producers) and extrapolations used to scale up regional to worldwide amounts (Piccinno et al., 2012; Gottschalk et al., 2011; Keller et al., 2013).

When released in natural media NPs will be subjected to a dynamic physical and chemical environment that consequently results in different and unknown endpoints far from their pristine or as released state. Therefore, environments and humans are not facing pristine manufactured NPs but rather transformed nano-enabled products, which is factually accepted but so far neglected. In fact, the large majority of the physicochemical and toxicity data obtained so far was focused on simple nanoscale particles and not on relevant nano-enabled products. This includes not only the NP embedded in the manufactured matrix but also the materials resulting from the interaction with biotic and abiotic (bio) molecules composing the natural systems. To further complicate the interpretation of the NPs studies, there are two distinct mechanisms that should be considered but are not easily differentiated: (i) chemical toxicity by the release of possible ions and/or formation of reactive oxygen species (ROS) (Fu et al., 2014), and (ii) physical stress or stimuli caused by NPs size, shape and surface properties (Vale et al., 2014; Libralato et al., 2013). These materials are generally associated with cellular perturbations such as ROS generation, and gene expression and proteome profiles alterations. For these reasons, the NPs escalating production and applications has raised concerns about their environmental and human safety, which have led to large investments in nanosafety-related projects resulting in a considerable amount of data assessing their potential hazard (Savolainen et al., 2013). However, the establishment of relationships between bioavailable NP-containing species and the specific bioadverse or biocompatible endpoints is still lacking, mainly since, the effects are NP-dependent and also specie-dependent (Buric et al., 2015).

This work provides an overview of the latest studies on the impact of NPs onto freshwater ecosystems, considered by many as the ultimate sink of these particles, with a special focus on (i) NPs transformations and characterization in the different test media, and (ii) toxicological effects such as generation of ROS, genotoxicity, metallomic and proteomic changes. This survey is focused on metallic NPs including nAg, $nTiO_2$, nZnO and nCuO, mostly due to the great number of studies dedicated to these particles.

2. NPs transformations in aquatic systems

NPs can enter in an aquatic compartment from (i) wastewater treatment plants effluents, (ii) direct use (e.g., application of NPs-containing paintings on boats), and (iii) deposition from the air compartment. When entering aquatic compartment, NPs will be exposed to a highly dynamic physical and chemical environment that leads to several transformations that will change their pristine or as released physicochemical properties (Fig. 1). These transformations, including dissolution, aggregation and sedimentation, are dependent on both physicochemical properties of the NP (and nanoforms thereof) and those of the environment into which they were released.

Colloidal particles, including organic and inorganic matter, are ubiquitous in the aquatic environment and can be originated from both natural and anthropic sources. These colloids can strongly interact with NPs, thereby determining their forms over space and time (dynamic speciation), and greatly affecting their bioavailability. Thus, the NP will have a specific speciation in each environmental compartment, and this speciation is always dynamic with reaction rates that depend upon the chemical nature and physical sizes of the engineered and natural colloids. Although it is clear that dynamic speciation must be considered in order to make relevant predictions of NPs fate, toxicity and risk, until now this critical issue, was mostly neglected (see detailed explanation on Pinheiro and Domingos, 2015).

Dissolution, which is one of the main transformations of metallic NPs such as nZnO, nCuO, and nAg, is mainly due to (i) the formation of partially soluble metal-oxide (Heinlaan et al., 2008; Domingos et al., 2013a; Wang et al., 2015), (ii) the oxidation of the particle constituents (Ma et al., 2014; Wang et al., 2013a; Dale et al., 2013; Lok et al., 2007; Derfus et al., 2004), and (iii) the complexation of the particle constituent metal by complexants present in the environmental compartment or even in the NPs embedded matrix (including the manufactured stabilizers) (Domingos et al., 2013b; Domingos et al., 2014). The sulfidation of the metallic NPs can retard their oxidation and, thus, their dissolution (Ma et al., 2014; Wang et al., 2013a; Dale et al., 2013; Thalmann et al., 2014). This dissolution mechanism results in the release of toxic cations, such that their persistence is reduced but the toxicity is increased. Evidently, complete dissolution of the NPs allows the prediction of their impact using already existing models for metal speciation and toxicity.

Photoreactions can also be important transformations affecting the NPs coatings, oxidation state, generation of ROS, and persistence, which is the case of the innately photoactive TiO_2 and ZnO particles (Hund-Rinke and Simon, 2006; Zhang et al., 2007a).

Aggregation is other critical transformation, which mainly by interaction with naturally occurring bio- or geomacromolecules affect NPs size and surface chemistry. For example, organic matter (OM) provides both charge and steric stabilization (Mohammed et al., 2008; Domingos et al., 2009a) of the NPs, although they may also result in bridging flocculation when in presence of multiple charged cations and anions (Domingos et al., 2010). OM effects are complex and difficult to predict, however, is of extremely importance to explore these interactions since, OM concentrations are typically orders of magnitude higher in concentration than engineered NPs, and, thus, likely to substantially modify their properties and behaviors. Despite the significance of these interactions, with both organic and inorganic matter, and to the best of our knowledge, no relevant toxicity studies are available.

Dissolution and aggregation are dynamic processes that can decrease the NPs available surface area, thereby decreasing their reactivity. However, this decrease is dependent on the surface properties, particle number, size distribution, and the fractal dimensions of the aggregate (Hotze et al., 2010). The NP size will affect its