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Review

Ecotoxicological effects of carbon based nanomaterials in aquatic organisms

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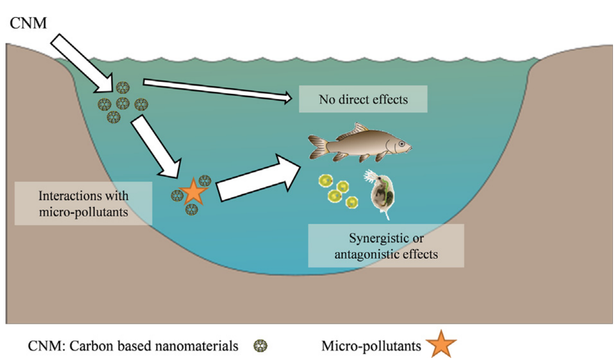
HIGHLIGHTS

- We review existing literature on the toxic effects of CNM in aquatic organisms.
- CNM are not toxic for aquatic organisms at environmentally relevant concentrations.
- Toxic effects of CNM are only observed at high concentrations.
- Ecotoxicity depends on the type of organisms, exposition time and CNM preparation methods.
- CNM modify the toxicity of other micro-pollutants.

GRAPHICAL ABSTRACT



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ABSTRACT

An increasing amount of carbon-based nanomaterials (CNM) (mostly fullerenes, carbon nanotubes and graphene) has been observed in aquatic systems over the last years. However, the potential toxicity of these CNM on aquatic ecosystems remains unclear. This paper reviews the existing literature on the toxic effects of CNM in aquatic organisms as well as the toxic effects of CNM through influencing the toxicity of other micro-pollutants, and outlines a series of research needs to reduce the uncertainty associated with CNMs toxic effects. The results show that environmental concentrations of CNM do not pose a threat on aquatic organisms on their own. The observed concentrations of CNM in aquatic environments are in the order of ng L^{-1} or even lower, much below than the lowest observed effect concentrations (LOEC) on different aquatic organisms (in the order of mg L^{-1}). Toxic effects have been mainly observed in short-term experiments at high concentrations, and toxicity principally depends on the type of organisms, exposition time and CNM preparation methods. Moreover, we observed that CNM interact (establishing synergistic and/or antagonistic effects) with other micro-pollutants. Apparently, the resulting interaction is highly dependent on the chemical properties of each micro-pollutant, CNM acting either as carriers or as sorbents, thereby modifying the original toxicity of the contaminants. Results stress the need of studying the interactive effects of CNM with other micro-pollutants at environmental relevant concentrations, as well as their effects on biological communities in the long-term.

Abbreviations: CNM, carbon-based nanomaterials; CNTs, carbon nanotubes; SWCNTs, single-wall; MWCNT, multi-wall carbon nanotubes.

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Contents

1. Introduction

Carbon-based nanomaterials (CNM) are allotropes of carbon with at least one dimension within the range of 1 to 100 nm. The main classes of CNMs that can be highlighted are buckyballs or spherical fullerenes (molecules with the atoms of carbon forming fused hexagons and pentagons organized as a hollow polyhedron), carbon nanotubes (CNTs) (cylindrical fullerenes) graphene (consisting one single layer of atoms disposed as a hexagonal lattice) and carbon black (amorphous carbon). Although a wide variety of buckyballs exist, with molecules from twenty to several hundreds of carbon atoms, the most commonly studied are C_{60} and C_{70} fullerenes (Klaine et al., 2012). Otherwise, carbon nanotubes are classified as single-wall (SWCNTs), double-wall (DWCNT) and multi-wall (MWCNT) carbon nanotubes, depending on the number of concentrically cylindrical walls that they present. The graphene family includes pristine graphene, reduced graphene and graphene oxide forms (Zhao et al., 2014). Finally carbon black is heterogeneous condensed aromatic and carbon-rich residue of incomplete combustion processes (Dickens et al., 2004). The origin of these materials is diverse, some can be released naturally to the environment (e.g., as a result of volcanic eruptions and forest fires), while others are produced during anthropogenic combustion processes, or are manufactured (i.e., engineered nanomaterials) (Navarro et al., 2008). The unique physicochemical, electronic and mechanical properties of CNM have triggered the commercial production of these materials. CNM are used in a wide variety of applications, such as water treatment, medical applications, optics, electronic engineering, photovoltaic devices, automotive industry, sports equipment and cosmetics (Bakry et al., 2007; Benn et al., 2011; De Volder et al., 2013; Jackson et al., 2013).

The widespread use of CNM has caused an increase of these materials into the aquatic ecosystems. Entrance pathways of CNM into aquatic systems include direct inputs, through the sewage and water effluents, as well as indirect inputs, associated to run-off events or atmospheric depositions (Mueller and Nowack, 2008; Nowack and Bucheli, 2007). In aquatic ecosystems, CNM can be accumulated in river sediments, or remain suspended in the water column and transported to the marine systems (Navarro et al., 2008). Although evidences of water contamination by CNM are rare, C_{60} has been detected in water samples from wastewater treatment plants in the range of ng L^{-1} (Bäuerlein et al., 2017; Farré et al., 2010; Wang et al., 2010). In this regard, wastewater treatment plants and effluents from factories producing nanoparticles are likely to be major point sources for contamination in aquatic systems (Holden et al., 2016; Scown et al., 2010), since wastewater treatment plants cannot guarantee the complete nanoparticles removal (Brar et al., 2010). Moreover, Gottschalk et al., 2009, 2013) estimated in a mass flow model, the most frequent values (modes) of concentration of C_{60} and CNT in Europe surface water as 0.017 ng L^{-1} and 0.004 ng L^{-1}, respectively.

The environmental behavior and effects of CNM in natural aquatic systems are related to their ability to interact and aggregate, creating clusters that exhibit a colloidal behavior. Despite the virtual water insolubility of individual CNM molecules, the formed aggregates are stable under certain environmental conditions. The properties of the aggregates (size, ζ-potential, shape, surface functionalization, sedimentation rate, critical flocculation concentration, etc.) are dependent on environmental parameters such as the pH, ionic strength, type and concentrations of dissolved organic matter and sunlight (Bundschuh et al., 2016; Handy et al., 2012).

The aquatic organisms can be potentially affected by the increasing occurrence of these nanoparticles. A key component for risk assessments of carbon nanoparticles includes an evaluation of their potential toxic effects to organisms and their potential bioaccumulation. Actually, evidences of ecotoxicological effects of CNM in aquatic organisms, as well as their availability to interact with other micro-pollutants through influencing the toxicity and bioavailability of co-occurring pollutants are still scarce. In this context, we have reviewed the current scientific literature on the toxicity effects of CNM in aquatic organisms. Finally, we have defined the most urgent research needs regarding CNM effects on aquatic ecosystems.

2. Methodology

We performed a literature review on the toxic effects of CNMs in aquatic organisms by using the Web of Science publications database. This review is focused on aquatic organisms exposed to water suspensions of CNM. We performed a literature search by combining the keywords “carbon nanoparticles” or “carbon nanomaterials”, with “aquatic organism” and “ecotoxicity”, “bacteria”, “algae”, “crustaceans”, “mussels”, “fish”, “amphibians”, “microorganisms”. A total of 176 studies were identified under the specified search terms for the period 2002–2017. For each publication, we compiled the year of publication, the involved test organism, the type of CNM, the time of exposure, the concentrations used, and the response variables. When available, we also collected toxicity endpoints such as the lowest observed effect