Analysis, behavior and ecotoxicity of carbon-based nanomaterials in the aquatic environment

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Due to their unique properties, carbon-based nanomaterials (CNMs) have attracted considerable interest in many fields of research, including materials sciences, microelectronics and biomedicine. The potential, the growing use and the mass production of fullerenes and carbon nanotubes have stimulated research on their potential impact on the environment and human health. To gather proper information about hazards of CNMs, it is important to have reliable analytical data on them, to find out how they behave in the environment and to evaluate ecotoxicological information about them.

This review presents the latest research carried out to assess the risks of engineered CNMs in the aquatic environment, including analytical methods and ecotoxicity assessment. We pay special attention to the surface properties of CNMs, which are vitally important for their aggregation behavior, their mobility in aquatic systems, their interactions with aquatic organisms, and their possible entry into the food chain. We also consider interactions with natural organic matter and other interactions that can alter aggregation behavior in water.

Keywords: Aggregation; Aquatic environment; Carbon-based nanomaterial; Ecotoxicity; Emerging pollutant; Environmental analysis; Human health; Mass spectrometry; Mobility; Surface property

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1. Introduction

Nanomaterials (NMs) are defined as materials that have structural features with at least one dimension of 100 nm or less, and include nanofilms and nanocoatings (<100 nm in one dimension), nanotubes and nanowires (<100 nm in two dimensions) and NMs (<100 nm in three dimensions) [1]. NMs differ in size, shape, composition and origin, and they can comprise organic or inorganic, crystalline or amorphous particles. They can be found as single particles, aggregates, powders or dispersed in a matrix, over colloids, suspensions and emulsions, nanolayers and films, and coated or stabilized as fullerenes and their derivates [2].

NMs can be classified in three main groups: (i) natural; (ii) incidental; and, (iii) engineered. Natural NMs are those that can occur naturally and may have been in the environment for millions of years (e.g., fullerenes have been detected in geological deposits from the Cretaceous-Tertiary boundary [3]). In addition, in a melt sample from an ice core dated as being about 10,000 years old, carbon nanotubes (CNTs) and fullerenes were detected in Greenland [4]. Nanodiamonds (NDs) have been also found in the Younger Dryas Boundary Sediment Layer in North America [5]. Incidental NMs are produced unintentionally during many industrial processes, or as consequence of engine pollution (e.g., welding fume and diesel-emission particulates are sources of incidental NMs). Finally, engineered NMs (ENMs) and nanostructures are produced intentionally and differ because they are being fabricated from the ''bottom up''.

During the past decade, interest in NMs has risen dramatically because of their exceptional physico-chemical properties. NMs are characterized by large surface-area-to-volume ratios, with about 40–50% of the atoms being on the surface; this results in greater reactivity, compared with bulk materials, or quantum effects. They are used in many industrial areas (e.g., materials science, personal-care products and electronics) and will provide a promising technology in many other areas (e.g., medicine [6]).

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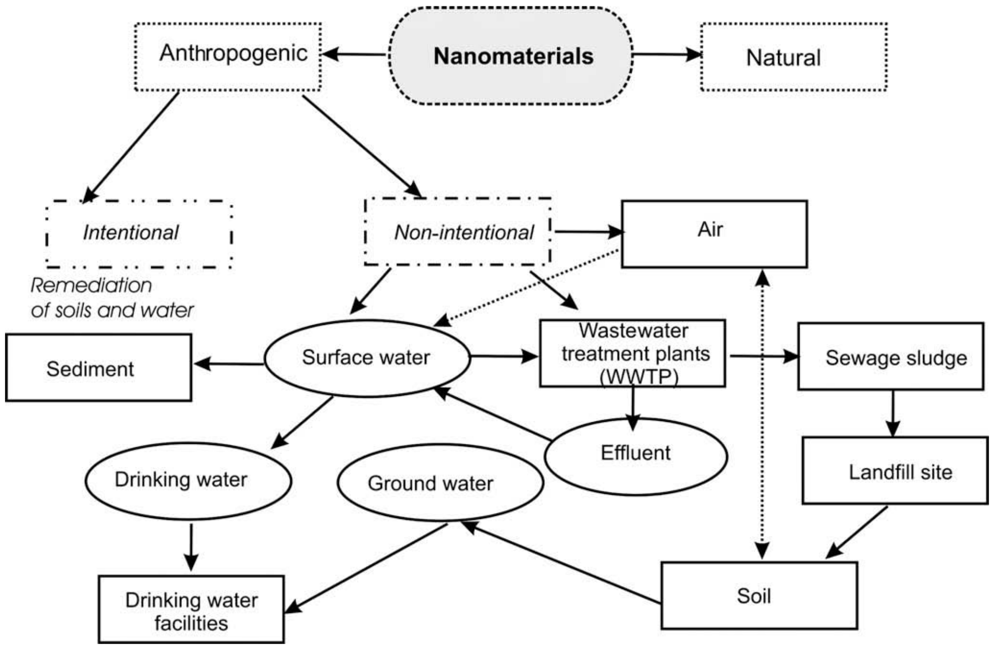

Figure 1. The fate of nanomaterials in the environment [11,12].

Classification of NMs for commercial purposes includes metal NMs, metal-oxide nanopowders, semiconductors and alloys, carbon-based NMs (CNMs) (e.g., fullerenes) and nanorods (CNTs and nanowires). In addition, nanolayers are the subject of the most important topics within nanotechnology. Through nanoscale engineering of surfaces and layers, a vast range of functionalities and new physical effects (e.g., magnetoelectronic or optical) can be achieved. Furthermore, nanoscale design of surfaces and layers is often necessary to optimize interfaces between different material classes (e.g., compound semiconductors on silicon wafers) and to obtain the special properties desired. Other supramolecular structures (e.g., dendrimers, micelles or liposomes) are also NMs [6].

At present, research on NMs is focused on development of new NMs or their applications in different areas (e.g., biomedicine [7]). However, concern has arisen about the presence of NMs in the environment. For example, the US Environmental Protection Agency (EPA) and the European Community (EC) are paying attention to the study of the fate, transport, and health effects of the NMs in the environment. However, their environmental study is still in its infancy because there is a lack of analytical methods able to detect and to quantify the wide range of NMs and their unique properties (e.g., there is only one paper available reporting fullerene concentrations in suspended solids of wastewater [8]). Also, NMs can be modified in the environment by the action of light, oxidants or microorganisms or can be coated with organic matter [9]. Moreover, NMs will inevitably aggregate or agglomerate into larger masses, thereby losing their nanoscale-related properties and increasing the difficulty of monitoring them in the environment. Although NMs are not yet regulated, they are already included in lists of emerging pollutants [10]. Through modeling a range of NMs arising from consumer products, estimations of the potential environmental concentrations have been published (Fig. 1 and Table 1) [11,12].

Because NMs are involved in a new technology and present properties different from common contaminants of larger dimensions, the risks of NMs have to be evaluated differently. Due to the great increase in the production volume and widespread use of NMs, they can pose a potential threat for the environment and human health. Since NMs differ in origin, size and material, NMs are expected to exhibit different biological effects. In addition, NMs of the same bulk material but with different crystal structure, surface coating or size can show different effects. For example, the toxicity of CNTs is affected by the degree and the kind of agglomeration [13].

Because only biological effects of NMs are known and no data on presence of NMs in the aquatic environment are available, their environmental risks are hard to predict. First simulations of environmental exposure of three NMs [i.e. silver, titanium dioxide (TiO_2) and CNTs] have been reported [12]. According to these calculations, CNTs presented no significant environmental risk. However, effects for TiO_2 and silver could not be excluded. Determination of these NMs in the environment is required for further risk assessment [14].

CNMs (e.g., fullerenes, CNTs and NDs) may be among the most useful ENMs for different applications. At present, fullerenes and CNTs are widely used, mainly in electro-optical devices, as polymers and films. CNTs can