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Review article

Carbon nanotubes: Impacts and behaviour in the terrestrial ecosystem - A review

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ABSTRACT

For more than twenty years, nanotechnologies have arisen a huge interest and are used in numerous fields. Carbon nanotubes (CNTs) are one of the most used nanomaterials thanks to their excellent optical, mechanical, electrical and thermal properties. All along their lifecycle, CNTs may be spread in the environment during production, use, destruction, reuse or potential accidents in production units or during transportation. For this reason, it is essential to evaluate their behaviour and potential impacts on ecosystems and particularly on the terrestrial ecosystem. After a brief summary of CNT properties, synthesis methods, and applications as well as detection and characterisation techniques, this review will focus on impacts of CNTs on the terrestrial ecosystem, discussing their behaviour in soil, plants and interactions with other pollutants as well as their impacts on soil microbiota, macrobiota and plants.

Contents

Abbreviations: CBNMs, Carbon Based Nanomaterials; UV–vis–NIR, Ultraviolet–Visible and Near-Infrared Spectroscopy; TEM, Transmission Electron Microscopy; AFM, Atomic Force Microscopy; SEM, Scanning Electron Microscopy; GC-MS, Gas Chromatography-Mass Spectrometry; GC-ECD, Gas Chromatography with Electron Capture Detector; EDS, Energy-Dispersive X-ray Spectroscopy; TGA, Thermo-Gravimetric Analysis; BET, Brunauer-Emmett-Teller; qPCR, Real-Time Polymerase Chain Reaction; Integrated PC/PT scanning cytometry, Integrated PhotoThermal and PhotoAcoustic scanning cytometry; ICP-MS, Inductively Coupled Plasma Mass Spectrometry; FTIR, Fourier Transform Infrared Spectroscopy; N.I, Non Informed Information; QD, Quantum Dot; DDx, DDT (dichlorodiphenyltrichloroethane) + DDE (dichlorodiphenyldichloroethylene) + DDD (dichlorodiphenyldichloroethane); MS medium, Murashige and Skoog medium; SWCNH, Single Wall Carbon NanoHorns; ROS, Reactive Oxygen Species; SPAOM, small polar aromatic organic molecules.

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1. Introduction

For more than a decade, nanotechnologies are more and more investigated by industrials and scientists and used worldwide for applications thanks to their remarkable properties. The European Commission defined in 2011 a nanomaterial as "A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions are in the size range 1 nm–100 nm" [1]. However, nanomaterial definition is different according to countries and to the field in which they are used. All definitions agree about the nanoscale dimensions but definitions differ on size distribution for example. This lack of global consensus is a serious challenge because it leads to legal uncertainty and differing regulatory for the same nanomaterial. The nanotechnology consumer products inventory (CPI) listed officially in 2014 more than 1800 consumer products containing nanoparticles worldwide. In less than ten years, the number of products containing nanoparticles increased by more than 3000% (54 products in 2005) [2].

Carbon-based nanomaterials are among the most used [2]. There are different types of carbon nano-objects such as fullerenes (3 dimensions < 100 nm), carbon nanotubes (2 dimensions < 100 nm, CNTs) and graphene and related materials (1 dimension < 100 nm). Since their discovery in 1991 by Iijima, they arose an extraordinary enthusiasm [3,4]. CNTs can be described as graphene sheets rolled over themselves to form (concentric) cylinders with a nanometric diameter. We can define three kinds of CNTs: single wall CNTs (SWCNTs), double wall CNTs (DWCNTs) with two concentric tubes and multi wall CNTs (MWCNTs) with more than two concentric tubes. CNT diameter varies from a few nanometers for SWCNTs to several tens of nanometers for MWCNTs. Their length is usually of a few micrometers. CNTs have remarkable optical, electrical, thermal, mechanical and chemical properties. They are used in numerous fields such as plastic additives, in batteries or some sporting goods [5].

It is essential to regulate production and uses of nanomaterials for a safe and sustainable future. So far there is no international agreement to supervise the production, use and commercialisation of nanomaterials. However, few countries started to monitor nanomaterials commercialised in their territories by using registers. In Europe, there is the European regulation for the recording, evaluation, authorization and restrictions about chemical substances (REACh). The recording and the authorization are compulsory for produced or imported nanomaterials with a volume of more than 100 tons. A new authorization protocol will be apply in 2018 for volumes between 1 and 100 tons, without toxicological data required. In theory, nanomaterials are covered by this regulation but practically they are often brought to the market without preliminary recording or monitoring. The first reason is that producers and distributors produce or import very rarely more than one ton per year, the threshold below which it is not compulsory to make a REACh recording. The second reason is that even if there is more than one ton per year, REACh does not oblige to record nanomaterials as new substances. Consequently, the recording gets an extension and the terms and conditions are simplified excluding for example ecotoxicological data. In France, a precursor in this domain, since January 1st, 2013, industrials and researchers have to declare annually the quantity, the properties and the uses of nanomaterials they produce or import in the R-Nano database handled by the ANSES (French Agency for Food, Environmental and Occupational Health & Safety) (L. 523-1 and L 523-3 of "Code de l'environnement" [6]). In Norway, since 2013, the national public agency of climate and pollution asks for identification of nanomaterials in the chemical product register. In Denmark, producers and importers have to record nanomaterials and products containing or releasing nanomaterials since 2014. Finally, in Belgium, since 2016 there is a royal decree concerning the placing on the market of manufactured nanomaterials.

In the USA, regulations for nanomaterials have been established by numerous organizations including the Environmental Protection Agency (EPA), Food and Drug Administration (FDA), and Consumer Product Safety Commission (CPSC). EPA is controlling nanomaterials by existing regulations of the Toxic Substances Control Act (TSCA) and Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) pursuant Significant New Use Rules (SNUR) of premanufacture notices (PMNs) of 13 chemicals, including CNTs and fullerenes. For nanomaterial manufacture and production, the manufacturers must inform the EPA with information about the nanomaterials within 90 days. For the FIFRA regulation, pesticide products containing nanomaterials must be registered. In Asia, the Japanese Council for Science, Technology and Innovation (CSTI) is paying attention to the new rules implemented in EU and USA. However, there is no legal control related to nanomaterial safety and environment so far. Anyway, Japanese Government is working with ministry of economy, trade and industry (METI) in order to collect information about the industry working with nanomaterials and to evaluate harmful effects of nanomaterials with the ministry of environment. Broadly speaking, scientists, associations and sanitary agencies are worried about the risks associated with nanomaterials and nanotechnology. However, industrials do not want regulatory framework because in the European and international market, nanotechnology is bringing jobs. So far, there is no strict regulation on nanotechnology. However, it is an international problem for environment, safety and health, it is thus essential to roll out international rules for their control.

All along their lifecycle, CNTs may be spread in the environment during production, use, destruction, reuse or potential accidents in production units or during transportation [7]. During their release, they can be subjected to physico-chemical modifications which may later modulate their potential toxic effects [8]. Toxicological studies evidenced that, CNTs present a potential risk for humans upon pulmonary exposure. CNT effects raise concerns because they can be compared to asbestos due to their fibre shape [9]. Asbestos caused a worldwide pandemia of disease in the 20th century such as asbestosis, mesothelomia, bronchogenic carcinoma, etc. [9]. For instance, Kasai et al. [10] studied the toxicity of MWCNTs with whole-body inhalation exposure in rats; they found that MWCNTs increased lung weight and inflammatory parameters of the exposed rats.

It is also essential to assess their behaviour and potential impacts on ecosystems. To date, the focus has been mainly on aquatic ecosystems rather than on the terrestrial ecosystems [11]. This review aims at summarizing the knowledge about behaviour and impacts of CNTs on the terrestrial compartment with a focus on plants. Our survey covered 71 studies on terrestrial ecosystems. The majority of the studies have been realized on plants (65%). Soil microorganisms and macroorganisms have been studied with respectively 14% and 17% of the studies. The less studied domain is the behaviour of CNTs in soil (in laboratory soil column) with only 4% of the mentioned articles. For plants, 46 studies have been published, with different culture conditions (Fig. 1a): most of the studies were based on plants exposed in a simplified media: hydroponics conditions (35%), filter paper (13%) and jellified medium (17%). Studies using soil exposure, representing the most relevant exposure scenario to mimic real environmental conditions, represent only 17% of the articles (15% in soil, 2% in sediment). The last part of the studies used *in vitro* tests on plant cells (16%). The exposure time is another parameter to take into account: among the 46 plant studies, 19% focus only on seeds (Fig. 1b). Most of the