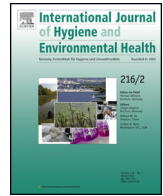




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Review

Human exposure to carbon-based fibrous nanomaterials: A review[☆]



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ABSTRACT

In an emerging field of nanotechnologies, assessment of exposure to carbon nanotubes (CNT) and carbon nanofibers (CNF) is an integral component of occupational and environmental epidemiology, risk assessment and management, as well as regulatory actions. The current state of knowledge on exposure to carbon-based fibrous nanomaterials among workers, consumers and general population was studied in frame of the International Agency for Research on Cancer (IARC) Monographs-Volume 111 "Some Nanomaterials and Some Fibres". Completeness and reliability of available exposure data for use in epidemiology and risk assessment were assessed. Occupational exposure to CNT/CNF may be of concern at all stages of the material life-cycle from research through manufacture to use and disposal. Consumer and environmental exposures are only estimated by modeled data. The available information of the final steps of the life-cycle of these materials remains incomplete so far regarding amounts of handled materials and levels of exposure. The quality and amount of information available on the uses and applications of CNT/CNF should be improved to enable quantitative assessment of human exposure to these materials. For that, coordinated effort in producing surveys and exposure inventories based on harmonized strategy of material test, exposure measurement and reporting results is strongly encouraged.

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[☆] *Disclaimer:* The findings and conclusions in this report are those of the authors and do not necessarily represent the views of institutions affiliated with the authors.

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1. Introduction

In 2014, an advisory Group of experts meeting every 5 years to recommend priorities for the International Agency for Research on Cancer (IARC), listed carbon-based nanomaterials [i.e. single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT), and carbon nanofibers (CNF)] as high priority agents to be evaluated for by the IARC Monographs Program. In October 2014, the IARC Monograph Volume 111 Working Group classified the well-characterized CNT sample Mitsui MWCNT-7 as “possibly carcinogenic to humans” (Group 2B) based on sufficient evidence in animal bioassays. CNT other than Mitsui MWCNT-7 were classified in Group 3 (“not classifiable as to their carcinogenicity to humans”) based on limited evidence in animal bioassays for MWCNT with physical dimensions similar to MWCNT-7, and inadequate evidence for SWCNT (Grosse et al., 2014). A Group 3 classification is not a determination of non-carcinogenicity or overall safety. It means that further research is needed, especially when exposures are widespread. It was the case for the CNT whose evaluation was done on the available published literature in which epidemiological studies are completely lacking. The recent production and/or use of the CNT and the latency time period potentially necessary between exposure to CNT and cancer development may not have been reached yet.

This review presents the current state of knowledge on exposure to carbon-based fibrous nanomaterials among workers, consumers and general population. More specifically, it aims at describing the exposed work population, the extent of the exposure in different target-populations, and the life-cycle steps of CNT/CNF-containing products of greatest exposure potential. The final goal is to address the quality of available exposure data in terms of completeness, precision and reliability for use in epidemiological and risk assessment studies as well as necessary improvements to fill the key data gaps.

2. Material and methods

2.1. Exposure agent

Depending on the process, the shape and physical and chemical characteristics (e.g. diameter, length) of the carbon based fibrous nanomaterial vary (Fig. 1). Because CNF may be produced as impurities during the CNT synthesis, both are often discussed together, as an issue of nomenclature.

2.2. Literature search and extracted information

PubMed and Scopus databases were searched for period 2000–2014 to identify studies dealing with exposure to CNT/CNF, excluding studies on medical application. References were searched using all combinations of keywords based on the following structure: “assessment” & “exposure” & “carbon nanotube”. The word “assessment” was alternatively replaced by “measurement”, “estimation”, and “modelling”. The word “exposure” was alternatively replaced by “release” and by qualitative adjectives describing the exposure, namely “human”, “occupational”, “environmental”, “consumer”, and “life-cycle”. The word “carbon nanotube” was alternatively replaced by the alternative names of

the carbonaceous nanofibers of interest, namely “single-walled carbon nanotube”, “double-walled carbon nanotube”, “multi-walled carbon nanotube”, “carbon nanofibers” and their abbreviations. References in papers were reviewed for additional sources. Relevant articles published in English in peer-reviewed journals were retained and classified by exposure origin, target population, and study approach (Fig. 2). The quality of the exposure measurement protocol and results reporting were reviewed, with a focus on the following parameters: exposure/release potential, exposure/release extent (amount) and unit of measurement, presence of CNT/CNF (specificity) and morphology of the released material.

3. Results and discussion

3.1. Exposure origin, pathway, and target populations during CNT/CNF life cycle

3.1.1. Occupational exposure

- *Research and development (R&D)*: academic and private laboratory workers are involved in the material conception, engineering and characterization. Laboratory workers usually work under experimental conditions with novel materials, instruments, and methods, so they may represent a distinct population with respect to potential occupational exposure.
- *Primary manufacturers*: workers at facilities producing CNT/CNF sold to researchers or industry.
- *Secondary manufactures*: workers at facilities purchasing CNT/CNF for the production of advanced materials (composite, thermoplastic materials) or for use in flexible panel circuits, lighting and other applications.

Many facilities are hybrid producer/professional users. They produce CNT/CNF and subsequently incorporate them into a product. Most facilities also perform developmental work on their own materials and products. For these reasons, R&D workers from primary and secondary manufacturers are considered together.

For workers involved in the manufacturing stage of CNT/CNF, the principal pathway for exposure is by inhalation of powder, or aerosolized CNT/CNF during production, formulation and packaging of product, and professional use of the CNT/CNF-enabling product (Table 1). Dermal exposure to spills or dusts from the production during the formulation process by secondary manufacturers is another likely pathway for occupational exposure.

3.1.2. Consumer exposure

Consumers might be exposed during normal use of CNT/CNF-containing products when mechanical, thermal, and biochemical interactions lead to product degradation. Environmental conditions of CNT/CNF composites uses influence the release potential; weathering is affected by moisture, salinity, pressure, temperature and light radiation, and will vary in marine or fresh water environments, or with altitude and biogeochemical conditions of exposure (Nowack et al., 2013). For example, CNT/polymer composite building will be subject to weathering stresses, and less to mechanical stresses. In contrast, a CNT/polymer composite used in laptop computer housing will be subject to mechanical stress (e.g. by scratching or cracking). In this case, the likelihood of release of free CNT/CNF is small because of the high-energy input needed. During

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