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Carbon nanotubes: Culprit or witness of air pollution?

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To the Memory of Dr Henri Szwarc, a dear friend and our best scientific advisor, whom we lost while preparing this manuscript. May his kind and witty soul rest in peace.

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ABSTRACT

The notorious $PM_{2.5}$ (2.5 μm diameter particulate matters) that can reach human lungs, considered as responsible for most deleterious effects of air pollution, are now unmasked. Anthropogenic carbon nanotubes and other carbon nanoparticles have been unambiguously identified as the major components of $PM_{2.5}$ in alveolar macrophages of Parisian children. Soot and diesel particulate matter have recognized detrimental health effects. However, information on the health effects of anthropogenic carbon nanotubes, which are the main components of $PM_{2.5}$ found within human alveolar cells, is still lacking. While nanotechnologists are focused on applications with a profit, notably in the field of nano-biomedicine, the health effects of nano-particulate pollutants attract little of their attention. In an attempt to bridge the research gaps between cutting-edge nanotechnologies, environmental studies and biomedical approaches, this opinion paper attempts to inform the nanotechnology community about critical issues related to airborne anthropogenic carbon nanotubes. The question that has to be urgently addressed is whether carbon nanotubes are the main culprit or act only as nano-vectors of carcinogenic polycyclic aromatic hydrocarbons and other toxic gaseous pollutants.

Common and widespread

Have you ever wondered what convenient Indian auto-rickshaws, powerful American heavy-duty engines and popular European (not necessarily German) cars have in common? They have all been reported to generate carbon nanotubes (CNTs) and emit them from their exhausts [1–3]. Carbon nanotubes, if an introduction is required, are cylindrical, sp^2-bonded carbon nanostructures that can be single- or multi- walled. As the building blocks of nanotechnologies, CNTs can be synthesized in a laboratory under controlled conditions, where rare structural defects and low impurity content result in unique and exceptional physical properties. Alternatively, CNTs can be made (less perfectly and less purely) outside the labs through different processes of common biomass combustion [4].

Diesel, the sustained source

Particles derived from biomass burning contribute to the major share of airborne carbonaceous particles. Among them, traffic-derived, especially diesel-derived, particulates (Fig. 1A), have been recognized as major particulate matter (PM) components [5]. Interestingly, in the opinion of the International Agency for Research on Cancer, based on the evidence of increased risk for lung cancer, diesel engine exhaust is carcinogenic to humans (Group 1). Be that as it may, according to the statistics published by the European Automobile Manufacturers Association (http://www.acea.be/statistics/tag/category/share-of-diesel-in-new-passenger-cars), the proportion of new diesel passenger cars continues to increase and currently represents more than 50% of sold vehicles. The roaming sources of diesel-derived particulates, including airborne anthropogenic CNTs [6], consequently, continue growing.

Commonality between ice core, ancient steel, and ... children

Carbon nanotubes appear as past [7] and present invaders of the atmosphere, and what is alarming is that they can reach our lungs as we have recently confirmed [8]. Inhaled CNTs (similar to those

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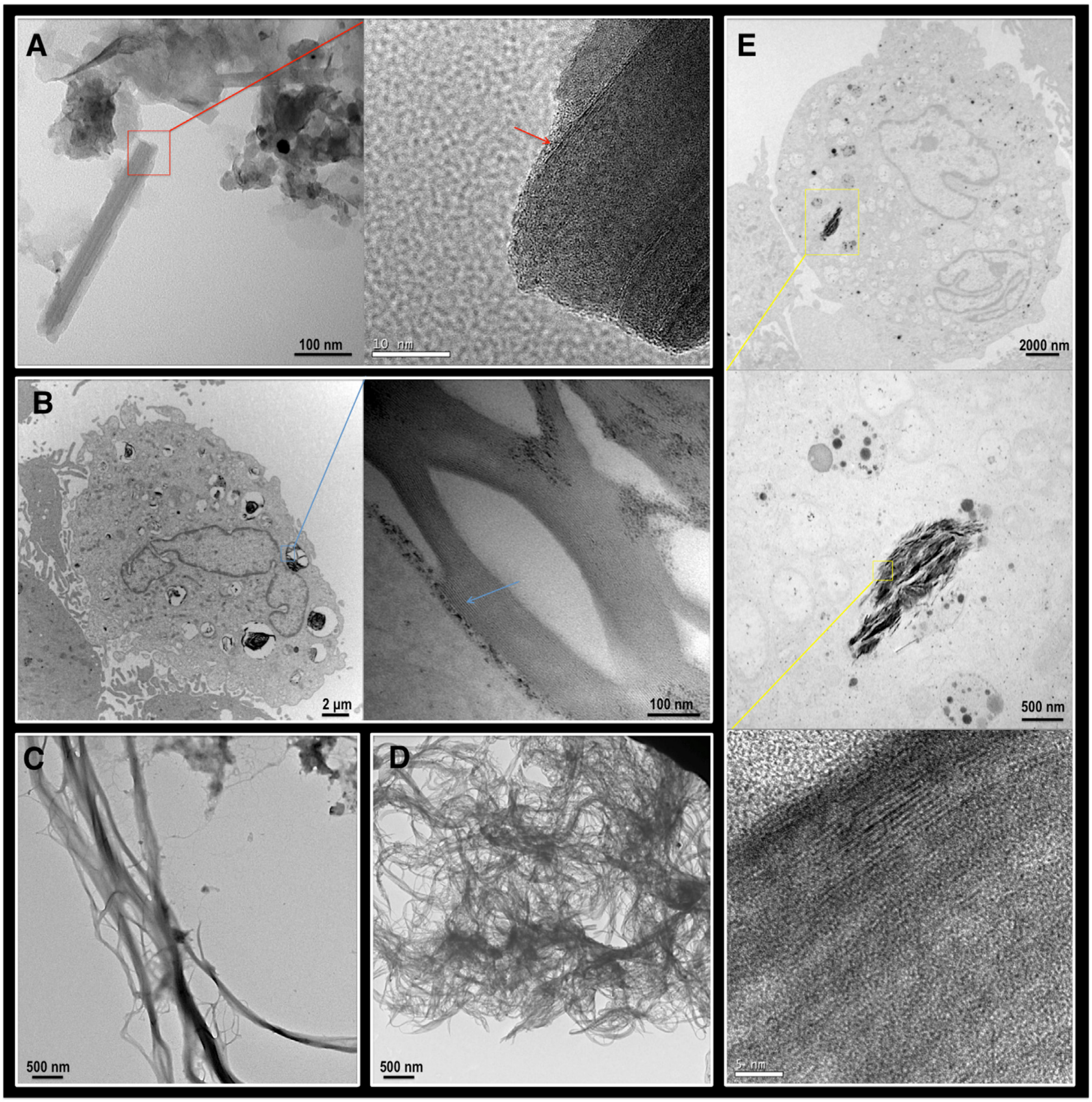

Fig. 1. Ultrastructural characteristics of airborne carbon nanotubes (CNTs) and surfactants: A) Left: diesel exhaust TEM micrograph showing spherical and CNT-like carbon nanoparticles and right: the HR-TEM micrograph of the red-squared zone confirming the structure of a multi-walled anthropogenic CNT, exhibiting a characteristic interlayer spacing of approximately 0.33 nm (red arrow); B) Left: A cell obtained from an asthmatic child, showing several black-appearing lamellar bodies, one of which (blue square) is magnified on the right: lamellar-body surfactant with its characteristic, graphite-like fringes (blue arrow); C) Filament-like structures obtained from broncho-alveolar fluid lysates, which become decreasingly electron-dense with the increasing electron microscope magnification (not shown on figure); D) Purified single-walled carbon nanotubes bundles, which remain electron-dense with the increasing electron microscope magnification (not shown on figure); E) From top to bottom: An alveolar cell containing CNT-like structures (yellow square), followed by its magnified TEM and HR-TEM micrograph, confirming the presence of graphitic layers characteristic for multi-walled CNTs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

collected in airborne dusts and vehicle exhausts) were present in all examined samples (N = 69) obtained from Parisian asthmatic children [8].

An unhealthy mix

Diesel-related health effects are vastly reported [9] and diesel soot particulates are recognized inducers of inflammation, immune response and oxidative stress [10]. Apart from primary diesel particles' intrinsic toxicity, atmospheric transformations, including reactions with OH radicals, ozone, NO_3 radicals and light [11], accentuate the toxicity. In addition, carbonaceous particles adsorb polycyclic aromatic hydrocarbons [12], which have an extensively documented carcinogenic effect.

By analogy, CNTs (as proven at least for synthetic ones), also interact with OH radicals [13], and exhibit increased toxicity when applied in combination with ozone [14]. While CNTs are associated with radical-scavenging activities, they also induce reactive oxygen species production within cells [15]. And, whilst they appear to be less toxic than carbon black and diesel particulates (*in vitro*) [16], CNTs also have a high adsorption capacity for polycyclic aromatic hydrocarbons [17].

Deceptive appearance

The idea that black carbon [5] penetrates the lungs is not new and was already proposed in a study performed on children from Leicestershire [18]. This study reported a strong dose-dependent link between the carbon content in alveolar macrophages and the

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