The Challenge: Carbon nanomaterials in the environment: New threats or wonder materials?

A new generation of carbon nanomaterials has emerged over the past decade—including carbon nanotubes, C60 fullerenes, graphene, and graphene oxides—and has attracted great attention from environmental scientists. Some of those materials offer opportunities to develop new tools for environmental applications (e.g., water treatment), but there are concerns related to the potential risks they represent for the environment and human health.

Should carbon nanomaterials be considered as new threats or new tools for the environment? Has a decade of intensive research enabled us to answer this challenging question yet? And if not, what hinders such assessment from being carried out? We have asked 3 authors to share their views on this controversial topic and to discuss what they believe are the most important remaining knowledge gaps and directions for future research.

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In Response: Views from research/academia on the challenges to detecting carbon-based nanomaterials in environmental matrices—An academic perspective

Since the discovery of C60 fullerene by Kroto et al. [1] and the progress of nanotechnology, a great effort has been made with respect to the development of carbon-based nanomaterials. These new nano-sized allotropes, such as carbon nanotubes (single-walled and multiwalled), nano-diamonds, and graphene, are currently in use in microelectronics, catalysis, battery and fuel cells, supercapacitors, conductive coatings, water-purification systems, plastics, and sensors, among other uses; and new formulations and applications are envisaged in the near future. Currently, however, the potential impact of nanotechnology in the environment and in human health remains unclear [2].

Previous reviews presented the state of the art in methods for the detection, quantification and characterization of nanomaterials, toxicology data, or toxicological evaluation. The present article aims to assess if current data and tools are appropriate in relation to the initial question: Are carbon-based nanomaterials wonder material or a new threat?

To establish the basis of risk assessment for carbon-based nanomaterials, realistic scenarios of exposure should be defined. To date, however, there is a lack of knowledge on their fate, transport, and behavior. One of the main drawbacks is the variety of environmental transformations and processes that can occur. For example, pristine fullerenes are highly likely to partition out of the aqueous phase and become adsorbed by biomass, particulate, and organisms. Pristine fullerenes also can be solubilized in colloidal aggregates, which can undergo transformation by the presence of organic matter, electrolytes, pH, and sun irradiation. Meanwhile, functionalized fullerenes are suspected of being transformed into more stable forms such as pristine homologos. Carbon nanotubes also can be solubilized and transformed by oxidative processes that modify their physicochemical characteristics. Therefore, combined approaches to characterize, identify, and quantify their degradation products are highly required.

To date, few analytical methods have been developed for the quantitation of carbon-based nanomaterials in the environment, and almost all of them were devoted to fullerenes. Most of these methods have been considered in different review articles [3,4], but in brief they are based on a separation step, generally by liquid–liquid extraction [5–7], solid-phase extraction [5–7], or filtration followed by ultrasound-assisted extraction with toluene [8,9] and then liquid chromatography coupled to mass spectrometry or tandem mass spectrometry. First studies in assessing fullerenes in the environment have been published during recent years [8–12]. For other types of carbon nanomaterials, however, such as carbon nanotubes, similar analytical approaches are not feasible because of their variable lengths and structures. Quantification at trace levels in complex samples has not been solved yet. In these cases, nowadays, their fate, behavior, and prevention of potential environmental impacts can be estimated only by means of models. Nonetheless, other difficulties that should be overcome are the lack of standardized approaches to characterize the toxicological behavior of nanomaterials. Among them are potential impurities present in the standards, the methods to prepare test suspensions, and toxicity test procedures. For example, nanomaterial suspension preparations can change the surface properties of nanomaterials or change their aggregation states with, in both cases, an
impact on the final toxicity. Moreover, toxicity tests designed for the toxicity evaluation of bulk materials are not suitable enough to assess the toxicity of nanomaterials in terms of end points and experimental design to avoid artifacts.

To build realistic models, uncertainty about which toxicological information should be incorporated and how to incorporate it must be overcome. More information on industrial releases, the percentage and form of used nanomaterials in final products, and their formulations should be considered together with the lessons learned from colloidal chemistry, long-term mesocosm studies, and results from similar nanomaterials that can be quantified in the environment, such as fullerenes. These objectives can be achieved only by means of interdisciplinary collaborations and with joint work between industry and research.

In addition, understanding the environmental impact of nanomaterials is a worldwide concern, and different initiatives have started in several countries. These include the European Union’s Seventh Framework Programme (FP7) and Horizon 2020 Framework Programme (previously named FP8) on nanotechnology and the US National Nanotechnology Initiative, among many others. The development of a common framework in terms of definitions of global standards, responsible development, and test methods aims at providing a better understanding of the potential impacts of nanomaterials.

There is a starting call for different regulations regarding products containing nanomaterials; but in addition, life-cycle studies should be carried out. If this new regulation is of interest for nanomaterials in general, it is outstanding for those nanomaterials that currently cannot be properly detected, analyzed, and assessed in the real environment, as happens with some carbon nanomaterials such as carbon nanotubes.

Future research should be considered with respect to the environmental fate and potential interactions with other contaminants present in the same compartments. In addition, it should be highlighted that, until now, researchers have struggled to deal with, in general, passive nanostructures; but active nanostructures are expected soon, followed by integrated and nano-systems [13]. Also, the question of how to assess their potential impact should be resolved.

The excellent properties exhibited by engineered carbon-based nanomaterials in new detection systems, novel wastewater treatments, and new remediation processes, among many other uses, provide merit to their consideration as new tools. To date, however, there is insufficient information about their potential environmental impact, and their sustainable use continues to be a potential threat. Integrated and multidisciplinary research studies and major industrial and regulatory involvement in international cooperation platforms are the required tools to overcome potential hazards. Therefore, in this context, uncertainty should be considered a synonym of risk.

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In Response: Measurement science challenges that complicate the assessment of the potential ecotoxicological risks of carbon nanomaterials—A governmental perspective

Although substantial progress has been made during the past decade toward understanding the potential ecotoxicological risks of some carbon nanomaterials, the data often were not obtained using standard methods, or, if standard methods were used, different modifications to the methods often were made. Current ecotoxicology standard methods are generally applicable for use with nanomaterials [1]; but nanomaterial-specific amendments will likely be needed and have not yet been agreed upon. Reproducible results obtained from robust, standardized methods will enable regulatory agencies to conduct a scientifically based risk assessment on carbon nanomaterials, a key step in the evaluation of the extent to which carbon nanomaterials represent a new threat to the environment at anticipated concentrations. This information will allow regulatory agencies to make scientifically informed decisions about the potential risks versus expected benefits of carbon nanomaterial use in various consumer products, such as carbon nanotube polymer nanocomposites [2,3]. The potential ecological effects of a single carbon nanomaterial have been reviewed [4]; the present perspective focuses on several measurement science topics that currently hinder ecological risk assessment of all carbon nanomaterials.
A lack of consistent nomenclature in the peer-reviewed literature complicates our understanding of the potential ecological risks of carbon nanomaterials. For example, single-walled carbon nanotubes can be called “single-walled carbon nanotubes,” “SWCNTs,” “SWNTs,” “CNTs,” or “carbon nanotubes.” This makes identifying all of the relevant literature unnecessarily complicated and time-consuming, and it also hinders use of databases to detect relevant trends. This situation is even more confusing for graphene, for which various terms are used, including as “graphene,” “graphene nanoplates,” “graphene oxide,” and “few-layered graphene.” One suggestion is for authors and journal editors to adopt internationally recognized standard terminology such as those published for carbon nanotubes by the International Organization for Standardization [5]. Although standard terminology for graphene is currently under development by the International Organization for Standardization but not yet available, the editors of Carbon have recently published a suggested terminology guide for graphene [6]. Other terms related to carbon nanomaterials, such as “purity” and “quality,” are often poorly defined and used differently by various groups.

Certain steps in protocols that may be robust for use with soluble chemicals may need to be more carefully specified for use with carbon nanomaterials as a result of the different behaviors and characteristics of carbon nanomaterials. One challenge in the standardization of ecotoxicity tests with carbon nanomaterials is that the elemental composition (primarily carbon) and unique shapes of carbon nanomaterials (rods, spheres, plates) complicate measurements of their dispersion state in aquatic media; many techniques (e.g., dynamic light scattering) utilize equations and assumptions based on spheres. Moreover, the polydispersivity of most carbon nanomaterials and the primarily carbon elemental composition hinder quantification measurements, especially in matrices with dissolved organic matter or in organism tissues, which also predominantly contain carbon [4,7]. Thus, making measurements of carbon nanomaterial concentrations is challenging and prone to artifacts [8,9], and there is often a lack of reliable analytical techniques to quantify concentrations in test media at low (micrograms per liter) concentrations. Whereas radioactively labeled carbon nanomaterials can be used in laboratory studies [10,11], additional work is needed to develop reliable analytical procedures for nonlabeled carbon nanomaterials. The lack of stability of carbon nanomaterial dispersions in aqueous media also complicates toxicity testing. In the absence of stabilizing agents, carbon nanomaterials often agglomerate and settle out of solution in aqueous test media typically used in nanocotoxicology experiments. This factor and the lack of reliable analytical methods hinder following standard ecotoxicological methods (e.g., Organisation for Economic Co-operation and Development test 202 [12]), which specify a change in concentration less than 20% during a several-day period.

Overall, research attention has focused predominantly on exploring the potential effects of carbon nanomaterials using various end points, with far less focus on determining the robustness and reproducibility of the test methods used for these measurements. Published results often are reported from a single experiment, and thus their repeatability is usually unclear [13]. Critical information for understanding the reliability of test methods, such as test method precision, robustness, reproducibility, and variability within and among laboratories, are rarely published for carbon nanomaterial ecotoxicity studies. For example, interlaboratory comparisons are needed to validate ecotoxicity tests with carbon nanomaterials, but only in vitro and rodent interlaboratory studies have been conducted thus far [14,15]. Research to improve the analytical rigor of ecotoxicity test methods for use with carbon nanomaterials thus represents a critical need to improve confidence in test methods and results and facilitate standardization.

Lastly, the form in which carbon nanomaterials will be released into the environment from carbon nanomaterial–enabled consumer products may differ from that typically used in nanocotoxicology tests. For example, carbon nanotubes in polymer nanocomposites may be fully or partly embedded in a polymer after release during degradation of a carbon nanotube polymer nanocomposite product [2]. Thus, ecotoxicological testing of pristine carbon nanomaterials may overestimate or underestimate their potential risks if carbon nanomaterials are released into the environment in a different form. Additional research is needed to assess the reliability of ecotoxicological test methods on the potential effects of carbon nanomaterials released from consumer products.

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In Response: Applications of carbon-based nanomaterials for water treatment—A business perspective

The water-treatment sector is a businessperson’s dream—a market that includes all living things, a product in unquenchable demand, and a severe supply shortage. Today, 780 000 000 people do not have access to clean water. By 2030, the United Nations predicts water demand will increase 40%, driven by increased withdrawals for agriculture, industry, and energy; if left unchanged, these trends are unsustainable. Given the scale of the possible humanitarian and economic impact, water is and will always be an enormous business, estimated at US $500 billion today and projected by Bank of America Merrill Lynch to hit US $1 trillion by 2020 [1]. The problem is very big, but the solution may lie in the very, very small—nanotechnology.

Over the past 20 yr, carbon-based nanomaterials—such as carbon nanotubes, C60 fullerenes, graphene, and graphene oxides—have been under the microscope; and much has been promised by these wonder materials, especially in water purification. Nanoengineering is opening up yet more frontiers for applying carbon-based nanomaterials to meet the challenges of water scarcity, particularly in the domain of filtration, where researchers are on the cusp of phasing promising experimental results into industrial adoption. Figure 1 shows a timeline for the development of various water-treatment technologies.

Of the viable routes to water purification, membranes are gaining widespread popularity because they require less energy and space and fewer chemical additives, and they can reject small ions and pathogens, yielding high-purity water from seawater or wastewater. The technology is relatively well established, led by industry heavyweights such as Dow, Pall, GE, 3M, Siemens, and Hyflux. The appeal of applying carbon-based nanomaterials in membranes stems from their intrinsic properties, including easy functionalization; organic chemical adsorption; mechanical durability; large, atomically smooth, and hydrophobic surfaces; nontoxicity; and environmental stability [2]. One established way that carbon-based nanomaterials have been applied to water-filtration membranes is as fillers in polymer matrix composites. For example, polymer membranes augmented with functionalized carbon-based nanomaterials (<10 wt% of the polymer mass) were shown to have increased surface hydrophilicity, mechanical properties, and durability in backwashing and reduced fouling, all with specific reference to treating oil-containing wastewater, something the shale oil industry regulates closely [3]. A more robust membrane thus may prove attractive to meet the market demand for water treatment.

In transitioning from the nanoscale to the useful macroscale, fiber-spinning techniques such as electrospinning present another exciting prospect. Carbon-based nanofiber mats can have their nanoscale porosities tuned and further cofunctionalized with nanoparticles. The results achieved in varying water-purification roles have been encouraging, including...
removal of harmful metal ions [4], adsorption and photo-/electrocatalytic activity in oxidizing organic contaminants and pathogens [5], antibacterial properties [6], and enhanced adsorption performance for electrodes in capacitative deionization desalination [7].

As of this writing, a cursory search has uncovered only 2 carbon-based nanomaterial–based water-treatment products, from Seldon Water and Porifera, both relatively young start-ups. For successful commercialization, a few milestones have to be met. First, the economics have to make sense; that is, the increased cost of using these materials must be balanced by the potential performance improvements. Second, the technical challenges with regard to producing these materials with consistency at large scales have to be addressed, which involves strengthening regulatory frameworks in safe manufacturing practices and establishing technical and quality assurance standards for products to be applied across the industry. A further prerequisite is the market demand for the product and presence of early adopters prior to the maturity of the technology, eventually culminating in a favorable environment to catalyze mainstream adoption.

As a frontier science, nanotechnology carries 2 special burdens: the weight of expectation and fear of the unknown. With the specter of the asbestos scandal shaking public confidence in regulatory systems, much has to be done to alter the perceptions of risk in relation to nanoscience by engaging in discourse regarding the safety of any nanomaterial-based products. Laboratory tests have been conducted to assess the potential toxicity [8], and standards have been established to regulate industry practices. The American National Standards Institute-Nanotechnology Standards Panel has published 42 standards under the International Organization for Standardization’s document ISO/TC 229 [9]. These steps go some way in assuring the public but address only the physical aspects of safety; for a nanotechnology business to succeed, it must address consumer psychology. The ubiquity of the microwave oven today belies the public’s initial hesitant response to the new technology. It was only after establishing their safety credentials and superior performance that microwave ovens achieved popularity. Nanomaterial businesses should seek to replicate this tenet of incremental acceptance from consumers. It will take brave pioneers to pave the way and win the hearts and minds of consumers—reputations are built on field experience and track records because laboratory test data can only do so much.

The introduction of carbon fiber is a good analog tracing the path to commercializing a modern material. When carbon fiber was introduced in 1970, early adopters were the military and aerospace industries, which are performance-driven and less sensitive to costs. Since then, industrial output has risen rapidly, and prices have dropped sharply. The automobile industry has just caught up. Catalyzed by environmental regulations, the lighter material improved the range of the car to meet the market need for electric transportation.

Many lessons can be learned from carbon fiber, the forerunner of carbon-based nanomaterials, in terms of courting early adopters. Industries need to be engaged in developing the technology further to maturity, where long-term gains justify short-term investment. Because water is a strategic resource, governments should also play a pivotal role in incubating start-ups, incentivizing industrial investment in emerging clean water technologies. The partnership between academia, the industry, governments, and entrepreneurs is vital in this endeavor.

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