



Nanopollution in the Aquatic Environment and Ecotoxicity: No Nano Issue!

Jayanta Kumar Biswas¹ · Dibyendu Sarkar²

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Nanotechnology: the New Revolution

Nanotechnology is the science and art of fabrication, manipulation, control, characterization, and use of smaller, faster, stronger and smart structures, devices, materials, or products with at least one dimension in the size range of 1–100 nm. It is regarded as one of the greatest human innovations, which has the potential to transform life and solve problems. The underlying truth behind the marvel of “novel and unique” physical properties is the science that as objects get smaller, they have higher surface area to volume ratio and greater interfacial nature. As a rapidly expanding and progressive field of research, nanotechnology has carved a promising niche in yielding a vast array of commercially available nanomaterials (NMs)/nanoproducts (NPs). NMs are defined as materials with at least one dimension between 1 and 100 nm. They can be carbon-based such as carbon spheres (e.g., fullerenes), carbon nanotubes, metal-based NPs, composite NMs or multilayer NPs (e.g., platinum core–silica shell), or NPs with capping or coating (e.g., functionalized zinc oxide NPs). Their novel properties have made them attractive for applications in diverse fields of information technology, energy production,

environmental protection, biomedical applications, food, agriculture, biotechnology, water treatment technology, and others, exemplified by a wide spectrum of products available in the market, including electronics, optics, textiles, medical devices, healthcare, cosmetics, food packaging, fuel cells, next-generation batteries, catalysts, biosensors, paints, self-cleaning windows, and stain-resistant clothing. The most common NMs in use are carbon (e.g., fullerenes, nanotubes), silver, silica, titanium dioxide, zinc oxide, and cerium oxide. During the last few decades, NMs and NPs available in the market have registered an exponential growth, and as a revolutionary platform technology, nanotechnology is predicted to become ubiquitous and expected to revolutionize the functionality of products.

Nanopollution: the New Face of Pollution and Ecotoxicity

As human society becomes attracted more towards harnessing potential benefits of nanotechnology, production of NMs, and generation and use of new-generation NP-enabled products increase. The exponential commerial growth of NMs finds significant reference of the European Commission's estimate of a global market of 11 million tonnes worth Euros 20 billion which has been projected to reach Euros 68 billion by 2020 [1]. Consequently, scores of synthetic/engineered NPs will emerge as new environmental contaminants because at the end-of-life of the NMs, they will end up in waste streams [2]. Nanopollution is a generic term for environmental contamination due to NMs during different phases of their life cycles from genesis to disposal. Disposed via domestic wastes or down the drain NPs start their journey and follow diverse routes to reach an environmental media, often a water body.

✉ Jayanta Kumar Biswas
biswajoy2008@gmail.com

¹ Enviromicrobiology, Ecotoxicology and Ecotechnology Research Laboratory, Department of Ecological Studies and International Centre for Ecological Engineering, University of Kalyani, Nadia, Kalyani, West Bengal 741235, India

² Department of Civil, Environmental and Ocean Engineering, Stevens Institute of Technology, 1 Castle Point on Hudson, Hoboken, NJ 07030, USA

Nanopollution is an “invisible” pollution and considered as the most difficult pollution to be managed and controlled [3].

Fate of NPs in the Aquatic Environment: Nano-Eco Interactions

The environmental fate and behavior of NPs including bioavailability, uptake, internalization, and toxicity are influenced by a range of physicochemical factors such as particle size, surface area, composition and oxidation state, coating, pH, EC, ionic strength, hardness, dissolved organic carbon, and humic and fulvic acids [4, 5]. Above all, ironically, it is the unique size-dependent properties of NPs which allow humans to exploit novel and incredible innovations, which could pose unexpected problems. At nano range, the properties of NMs differ substantially from the bulk materials due to the increased specific surface area and reactivity, which may lead to amplified bioavailability and toxicity [6, 7].

The most important processes affecting NPs' fate in aquatic systems are agglomeration and aggregation, dissolution, redox reactions, and transformation into new solid phases [8]. Aggregation results from interaction between two mobile objects, whereas deposition is the attachment of a mobile particle to an immobile phase. In agglomeration, particles are held together by weak van der Waals forces, while in aggregation by strong chemical bonds or sintering. The surface properties of NPs play pivotal roles in influencing their stability and mobility as colloidal suspensions or their aggregation into larger particles, and consequently how they are removed from the water column, transported, adsorbed, and/or transformed in the sediments [9]. Thus, sediments serve as significant sink for synthetic NPs while benthic organisms act as their key receptors. Factors like pH and concentrations of different ions and organic matter influence agglomeration rate [6, 10]. The environmental fate and bioavailability of NPs depend on their interactions with aquatic colloids. Humic and fulvic acids influence the suspension stability by interacting with the surfaces. Dissolution reactions lead to the release of toxic ions [11]. Synthetic NPs may sorb other toxicants (e.g., phenanthrene) and amplify the latter's toxicity through potentiation.

Nano-Bio Interactions and Toxic Effects: When Small Is Big

Since man-made NPs do not naturally appear in nature, organisms may not have appropriate defensive means and mechanism to deal with these invisible nano-invaders. The surface properties of NPs and their biocompatibility depend on the charges carried by the particle and its chemical reactivity. The routes of exposure and uptake of NPs by aquatic organisms include dermal, ingestion, inhalation through skin, diet, and gills. Filter feeder animals (e.g., forage fishes,

crustaceans, and molluscs) feeding on suspended matter and food particles from water are particularly vulnerable to exposure and uptake of NPs dispersed in the water column. Bottom dwelling and benthivorous animals (*Chironomus* sp., *Arenicola* sp.) and biofilm feeders may be more prone to be affected by sediment NP exposure. Several kinds of endocytic pathways have been proposed for incorporation and internalization of NPs in cells via endocytosis: clathrin-mediated endocytosis, caveolae-mediated endocytosis, macropinocytosis, and phagocytosis [12]. Some synthetic nanoparticles may be directly toxic to aquatic organisms. For example, AgNPs released into the environment may erode ammonia-oxidizing bacteria, and thus affect nitrification due to silver ion released. The detrimental effects of CuO NPs on soil microbial community were expressed in terms of reduced hydrolytic activities, dehydrogenase oxidative potential, and community composition [13].

When NPs come in contact with biological fluids, they immediately interact with the biomolecules present [14]. This alters the physicochemical properties of the NP, by affecting their zeta potential, their size, and the functional groups, but also affects the biological functioning of the bound biomolecules [15]. The binding of proteins and other biomolecules to NP is strongly driven by electrostatic forces and direct interaction of functional groups with the metal surface. This specific interaction can alter cellular and biochemical functioning by blocking binding domains of ligands, cofactors, or DNA, or by inducing conformational changes in proteins. Metal and metal oxide NMs having catalytic nature (e.g., titanium dioxide) mediate chemical reactions that generate toxic-free radicals or reactive oxygen species (ROS) which are extremely reactive and highly unstable, and attack and snatch energy from available cell molecules [5, 16]. In the process of oxidative stress, ROS modifies biomolecules and induces lipid peroxidation, oxidative protein denaturation, and DNA damage [5, 17]. These ROS are also known to damage cell membranes, and inflict toxicity on many aquatic organisms. Acute to chronic exposure to CuO NPs and Fe₂O₃ NPs results in ROS production and affect the antioxidative defense system of aquatic organisms. Altered expressions of biomarker profile of antioxidant molecules and enzymes (glutathione, SOD, CAT, POD, GPx, SeGPx, GST, and GR) are indicative of nanoparticle-induced oxidative stress [18]. Significant histopathological damages, hematological, reduced growth, embryo mortality, hatching delay, teratogenic malformations, and neurotoxicity have been reported in fish juveniles [19]. In bacteria, NPs disrupt their rigid cell wall and cytoplasmic membranes, changing the membrane permeability, which increases entry into and interactions of NPs with DNA and protein. Sparingly soluble NPs (e.g., cobalt oxide and manganese oxide) enter into cells by a Trojan Horse-type mechanism, i.e., metal oxide NPs enter into the cells but not the respective ionic forms [20]. Once in the cell, these NPs may

dissolve releasing higher detrimental concentrations of metal ions within the cell.

Knowledge Gaps and Future Scope of Research

Developments in nanotechnology are leading to a rapid proliferation of new materials in the environment, where their possible ecotoxicological impacts remain unknown. Given the growing variety of NP interacting with the diverse aquatic species under complex aquatic regime, an urgent need for sound nanoecotoxicological risk assessment is to understand the mechanisms that govern the fate and toxicity of NPs in aquatic environments and their interaction at the nano–bio–eco interface with an emphasis on the quantitative structure–activity relationship (QSAR) [21, 22]. Since the water column in lakes and marshes is heterogeneous in nature with variations in pH, Eh, dissolved oxygen, salinity, hardness, ionic strength, or organic ligands, and other physicochemical parameters, researches on the fate of NPs in the aquatic environment should take into account the relevant aspects of limnology and biogeochemistry. To date, there have been little systematic ecotoxicological studies investigating influence of changes in such water chemistry on ecotoxicity of NPs. The problem becomes more complex, because nanoparticles can significantly change their structure, shape, and size as a result of aggregation, solubilization, or adsorption phenomena. Despite a little preliminary studies, synergistic effects due to simultaneous exposure to multiple nanoparticles as well as toxic effects from genetic to systemic levels are not yet well known, and further research should be carried out to fill this knowledge gap. There is little information on role of NPs as vectors of chemicals, microorganisms, and their interactions with other stressors. Examination of the distinct contribution of the particulate and dissolved forms of NPs in both the abiotic environment and biota is of great significance for framing regulatory norms and risk assessment. Majority of the nanotoxicological studies undertaken so far are descriptive or “proof-of-principle” experiments which have tried to document toxic effects on individual organisms, bearing hardly any concrete ecological implications. Indeed, nanoparticles accumulated by primary producers could be transferred to the successive trophic levels, leading to cascade and ripple effects. To bridge the huge knowledge gap, an urgent need is to undertake comprehensive studies for unveiling interactions and effects of NPs on different species belonging to different trophic levels of the aquatic ecosystem, including bacteria, phytoplankton, zooplankton, and fish, their toxicological responses from genetic to systemic levels, and fate of NPs along the food chain and food web of the ecosystem.

Compliance with Ethical Standards

Conflict of Interest Jayanta Kumar Biswas declares no potential conflicts of interest.

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