Chapter 6
Risk Assessment and Toxic Effects of Exposure to Nanoparticles Associated with Natural and Anthropogenic Sources

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Abstract Humans have been exposed to airborne particles, especially to nanoscale particles, during their developing period, but this exposure has increased enormously over the last century due to anthropogenic sources. This increase is due mainly to combustion processes where these particles are released to the environment unintentionally but the rapidly growing field of nanotechnology is likely to become yet another source for such very small particles. Nanoparticles are natural products but their tremendous commercial use has encouraged the synthesis of these fine and ultrafine particles. Accelerated production of these particles may lead to increased risks to humans and the environment. Therefore, a detailed understanding of their sources, release interaction with environment and possible risk would provide a basis for safer use of engineered nanoparticles with minimal or hazardous impact on environment. Each of these particles carries different blends of chemicals and therefore poses a different health risk. Keeping all these points in mind the present work provides up to date information on sources, different types of interaction with environment and possible strategies for risk management of nanoparticles. An understanding makes a major contribution to the risk management that is needed to ensure that utilization of nanoparticles is made safely, is exploited to their full potential and disposed off safely.

6.1 Introduction

Airborne nano and microparticles are important for atmospheric chemistry and physics. It is also important for the biosphere, climate and public health. They influence the Earth's energy balance, the hydrological cycle and atmospheric circulation and the abundance of greenhouse and reactive trace gases. Moreover, they

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M. Gupta Bhowon et al. (eds.), *Chemistry: The Key to our Sustainable Future*,
DOI 10.1007/978-94-007-7389-9_6,

play important roles in the reproduction of biological organisms and can cause or enhance diseases such as oxidative stress, hypertension, allergy and asthma. The primary parameters that determine the environmental and health effects of aerosol particles are their size, composition and concentration. These parameters, however, are spatially and temporally highly variable.

Particulate matter (PM) is a complex mixture of natural or geological particulates, natural soot or carbonaceous matter, and a host of anthropogenic or man-made particulate matter which includes a plethora of combustion particulate matter (including from power generation, agriculture burning, transportation, erosion and wear debris from paints and coatings, fire and pavement wear, other secondary reaction products and a wide range of biogenic PM). These PM include nanoparticulates ranging from one to several hundred nanometers in diameter to primary particulates. Aggregates are categorised and they are defined as ultrafine, fine and coarse PM as $< PM_{0.1} < PM_1 < PM_{10}$ [1, 2], whereas very small particles with size ranging 1–100 nm are called nanoparticles. Nanomaterial means an insoluble or biopersistent and intentionally manufactured material with one or more external dimension or an internal structure, on the scale in the range 1–100 nm [3]. According to EU the nanoparticles are defined 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 is in the size range 1–100 nm [4]. It has the ability to enter translocation within and damage living organisms. This ability results primarily from their small size, which allows them to percolate psychological barriers and travel within the circulatory systems of a host. Nanoparticles in the atmosphere may be present due to release directly from a source (primary emissions) as nanoparticles or formation as a result of reactions in the atmosphere (secondary emissions). Global pollution is estimated to cause roughly 40 % of deaths worldwide [5]. While ultrafine or nanoparticles account for <1 % of general outdoor mass abundance of PM, they account for a significant fraction (>90 %) of the PM abundance or number concentration [6].

Nanoparticles generally have been demonstrated to be associated with adverse respiratory health issues in contrast to the larger size PM, where the number concentrations are smaller while the corresponding mass concentrations are much greater [7, 8]. The air in different micro-environments already contains varying concentrations of different kinds of small airborne particles that are regarded as pollutants. Large scale epidemiological studies confirm the relationship between exposure to airborne particles and mortality in cardiopulmonary diseases. Increased attention is directed at airborne nanoparticles in our indoor environments. The reason for this is the increased application of nanotechnology for new materials possessing attractive mechanical, electrical, magnetic and optical properties. A large increase in such materials could, when they are handled, give rise to an increase in the concentration of nanoparticles in air in different environments. There is concern that there is a risk of health effects when humans inhale these particles [9–11] and also causing cardiovascular disease in humans, such as chronic obstructive pulmonary disease (COPD) and asthma in children and compromised adults

[12–14]. To identify nanoparticles, exposure scenario that may occur during the whole life cycle from production to use of manufactured nanomaterials is an important component of the overall risk characterization and management programme [15]. The characterizations of nanoparticles in terms of mass and number concentration, chemical composition, physical and chemical properties and their sources are necessary to identifying their effects on human health and environment. Therefore the present article provides information on sources, different types, interactions with environment, chemical composition and possible strategies for risk management of nanoparticles.

6.2 Types of Nanoparticles

Figure 6.1 shows the size and scale of nanoparticles and based on dimensionality, morphology, composition, uniformity and agglomeration, the nanoparticles are classified into the following categories:

- 1D nanoparticles (nano fibers, rods and carbon nanotubes (CNT))
- 2D nanoparticles (nanocoats and nanofilms)
- 3D nanoparticles such as polycrystals

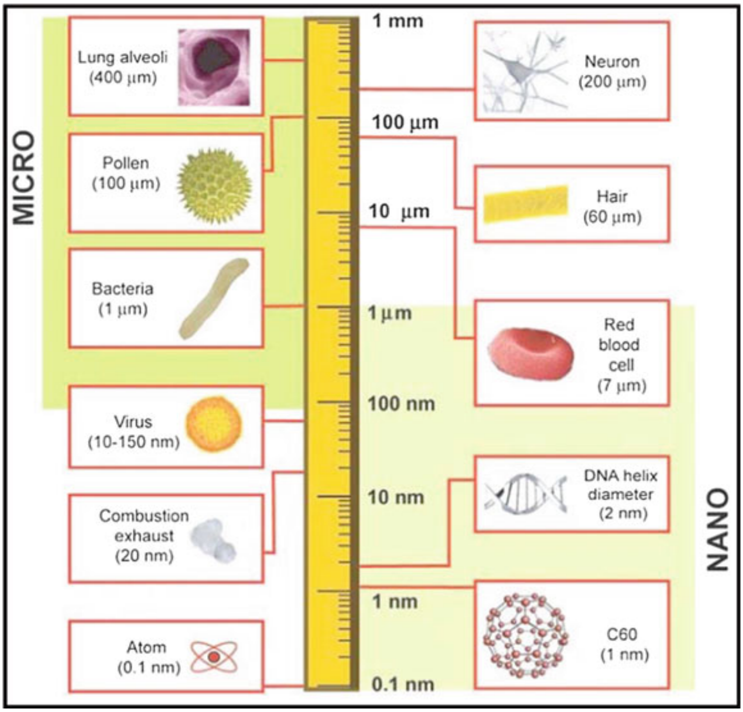

Fig. 6.1 Length *scale* showing size of nanomaterials compared to biological component [16]

- Nanotubes
- Nanowires
- Magnetic nanoparticles (dispersed aerosols, suspension/colloid)
- Engineering nanoparticles

6.3 Sources of Nanoparticles

The composition and mass concentrations of nanoparticles in clean background areas are strongly affected by long-range transport. During transport and aging, particles of different origin may change their properties due to coagulation and cloud processes as well as due to reactions with gases via various heterogeneous pathways [17]. The origins of these particles can be natural as well as anthropogenic.

6.3.1 Natural Sources

Nanoparticles are abundant in nature, as they are produced in many natural processes, including photochemical reactions, volcanic eruptions, forest fires, simple erosion and by plants and animals, like shedding of skin and hair. Though we usually associate air pollution with human activity such as automobile industry and charcoal burning, natural events such as dust storm, volcanic eruption and forest fire can produce such a quantity of nanoparticulate matter that they profoundly affect air quality worldwide. The aerosols generated by human activities are estimated to be about 10 % of the total, the remaining 90 % having a natural origin [18].

6.3.2 Anthropogenic Sources

Humans have created nanoparticles, as they are the by-products of simple combustion (with sizes down to several nm), food cooking, chemical manufacturing, welding, ore refining and smelting, combustion in vehicle and airplane engines [19], while engineered nanoparticles are commonly used in cosmetics, sporting goods, tyres, stain-resistance clothing, sunscreens, toothpastes and food additives. These nanomaterials and new more deliberately fabricated nanoparticles, such as carbon nanotubes, constitute a small minority of environmental nanomaterials [20]. Epidemiological studies conducted on diesel locomotive drivers showed a correlation between occupational exposures to diesel engine exhaust and incidence of lung cancer in the workers [21]. Long term exposure to indoor cooking emissions may pose adverse health effects due to particulate matter inhalation. During cooking, the level of particulate matter increases more than tenfold compared to non-cooking hours [22]. In developing countries, approximately half of the world population and up to 90 % of rural households still used the unprocessed biomass fuels such as wood, dung and crop residues for cooking. In the energy ladder, these biomass fuels which are known as dirtiest fuels lie at the bottom of the energy ladder. It is also found that about 78 % of Indian population relied upon the biomass fuels and 3 % on coal for cooking. Moreover, the stoves or chullas which are used for cooking are not energy efficient and the fuels are not burned completely. The incomplete combustion of biomass releases complex mixtures of organic compounds such as particulate matter, carbon monoxide, polyorganic material, polyaromatic hydrocarbons and formaldehyde. It is estimated that about half a million women and children die each year from indoor air pollution which are emitted from biomass fuels used for cooking in India. On comparing these data to other countries, India has among the largest burden of diseases due to the use of dirty household fuels and 28 % of all deaths due to indoor air pollution in developing countries occur in India [23–25].

In many regions of the world, death caused from indoor smoke from solid fuels is considerable, especially in Asia and Africa. World Health Organization estimates that more than 50 % of the world population uses solid fuels for cooking and heating, including biomass fuels [26].

6.4 Nanotoxicology

Human skin, lungs and the gastro-intestinal tract are in constant contact with the environment. The lungs and the gastro-intestinal tract are more vulnerable while the skin is generally an effective barrier to foreign substances. These three body parts are the most likely points of entry for natural or anthropogenic nanoparticles. Injections and implants are other possible routes of exposure, primarily limited to engineered materials. The possible adverse health effects associated with inhalation, ingestion, and contact with nanoparticles depend on various factors including size, aggregation, crystalline and surface fictionalization. Figure 6.2a, b show the publications in the field of nanomaterials or ultrafine particles and their toxicity.

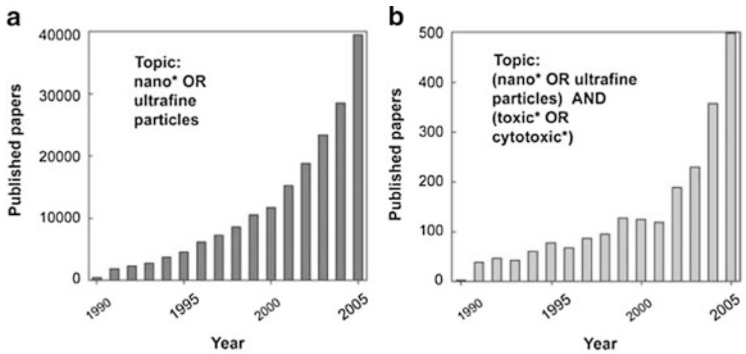

Fig. 6.2 (**a**) and (**b**) Statistics on scientific articles published on (**a**) nanomaterials and (**b**) their toxicity (ISI Web of Science) [16]

6.5 Characteristics of Particles

6.5.1 Size and Agglomeration

Nanoparticles such as engineered nanoparticles, unintentionally created nanoparticles, and ambient ultrafine particles are smaller than 100 nm in diameter (Fig. 6.3). Their physical and chemical characteristics are as varied as the processes that create the particles [22]. As the particle size becomes smaller, a greater fraction of atoms are at the surface and quantum effects tend to increase the surface reactivity. At the same time, nanoparticles have a tendency to agglomerate and form larger structures. Thus, agglomeration can lead to a reduction in the number of atoms at the surface with a reduction in surface energy.

6.5.2 Particle Shape

Prior experience with asbestos and other fibrous aerosols indicates that the shape of the particles (i.e. their length and diameter) has a profound effect on toxicity. Smaller diameter fibers penetrate deeper into the respiratory tract, while longer fibers are cleared more slowly [27, 28]. Engineered nanoparticles come in various

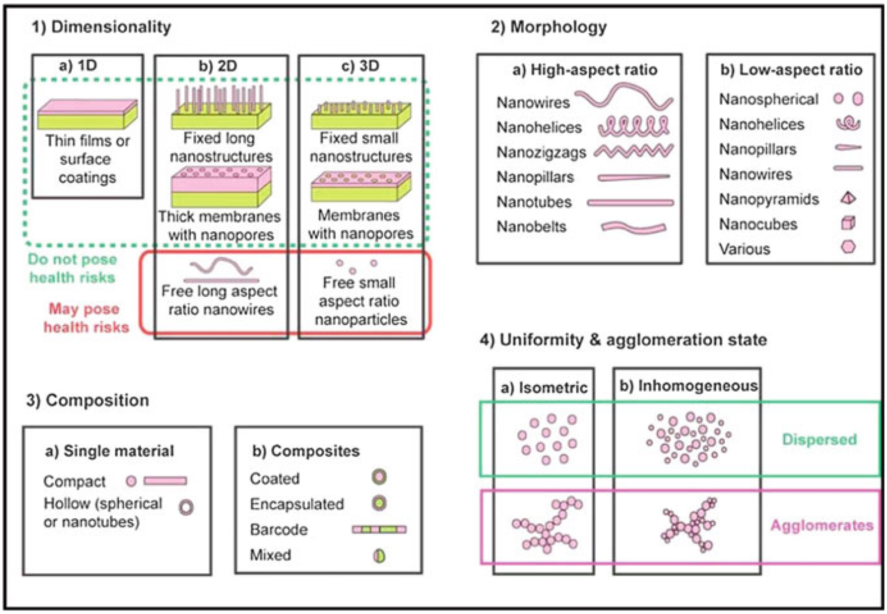

Fig. 6.3 Classification of nanostructure materials based on dimensions, morphology, composition, uniformity and agglomeration state [16]

shapes such as spheres (e.g. dendrimers), tubes (e.g. single wall carbon nanotubes (SWCNT) and multi wall carbon nanotubes (MWCNT)), plates (e.g. nanoclay flakes), fullerenes, and needles. In the human body it seems that the deposition, fate and toxicity of the particles will be affected by the shape of the particles [29].

6.5.3 Chemical Composition

The chemical composition of particulate matter is an essential information for assessment of its sources and health effects [26]. The chemical composition of the surface and the bulk of engineered nanoparticles will affect toxicity (Fig. 6.3). Surface coatings that modify the agglomeration properties of nanoparticles can also have biological effects [30, 31]. Experiments using fullerene soot with different impurities (e.g. metallic endohedral fullerene) indicate that the pulmonary toxicity response depends on the type of nanomaterials and their impurities [32].

6.6 Importance and Interaction of Nanoparticles in Environments

The risk associated with exposure to engineered nanomaterials (ENM) will be determined in part by the environmental processes that control fate, transport and transformation. The toxicity of environmental nanoparticles (ENP) depends upon the exposure levels of the nanomaterials during transformation from one ecosystem to another ecosystem. Atmospheric nanoparticles are of growing interest to many investigators for two main reasons. First, nanoparticles are important precursors for the formation of larger particles, which are known to strongly influence global climate, atmospheric chemistry, visibility, and the regional and global transport of pollutants and biological nutrients. Second, atmospheric nanoparticles may play critical roles in the deleterious human health effects associated with air pollution. In addition to these two well-recognized roles, nanoparticles may also significantly influence the chemistry of the atmosphere. Because their composition and reactivity can be quite different from larger particles, the presence of nanoparticles may open novel chemical transformation pathways in the atmosphere. There are possibilities that an important role for nanostructures can be visualized within larger particles, which often contain nano-scale features such as mineral grain agglomerates, soot spherules, or layer coatings of sulfates and nitrates. These complex morphological features likely influence a number of properties. For example, nanostructures probably affect water uptake via capillary condensation and nanoscale aqueous surface films may provide a medium for heterogeneous chemistry. In addition, nanoscale active sites on surfaces may influence particle phase transitions through heterogeneous nucleation.

However, with a few notable exceptions, the potential roles and implications in atmospheric chemistry for nanoparticles and nanostructures have not been quantitatively examined.

6.7 Risk Assessment of Nanoparticles

Research on the effects of particulate matter on human health was initiated in the 1970s [33] and has been strongly developed since then. It indicates that small particles cause serious problems to human health, contributing to increased mortality and sickness [34]. The mechanisms underlying these adverse effects are not well understood and major questions concerning the species size fraction, chemical composition, and causative mechanisms leading to the observed health effects remain [35]. This is partly due to results from epidemiological surveys showing that there is a correlation between the mass concentration of particles and mortality and hospitalization [36]. From a health perspective, the size of the particles is important as it affects their ability to penetrate into the lungs and cause adverse health effects. The larger particles (e.g. those greater than 10 μ) tend to settle in the nose and mouth and are unlikely to pose a health risk [37]. However, ultrafine particles (i.e. diameters less than 0.1 μm) are considered especially detrimental to human health, since these particles can be inhaled and deposited deep in the alveoli of human lungs [38]. It has been increasingly recognized through epidemiological investigations that particulate matter in agricultural air contributes to the progression and exacerbation of respiratory diseases (such as asthma and other ailments), and in urban air leads to an increase in morbidity and mortality from respiratory and cardiac conditions [39]. Children's susceptibility to health problems as a result of exposure to air pollution is of concern. Children may receive an increased dose of particulate matter to their lungs compared to adults [40]. Moreover, PM has been linked to cancer and premature death [41].

Nanoparticles have been reported to potentially induce adverse health effects [6, 42, 43] and the need for thorough risk assessment has been identified [44]. The risk of nanoparticles is not only a function of their potential hazard, but also of exposure thereto. Assessing the exposure to the nanoparticles at workplaces during nanoparticles production is therefore one important step towards a sustainable nanotechnology [45].

A health risk assessment has to consider data from various lines of evidence (e.g. human epidemiological and clinical studies, experimental animal and in vitro studies, *in silico* studies) and integrate these into a cohesive evaluation. It is furthermore essential to have relevant information on exposure. A risk can then be deduced from exposure data together with the hazard assessment. Needless to say, the assessment becomes more reliable when more relevant information is available. Data on assessment of human exposure to ENPs are very sparse. However, there is at present very little reason to expect that the general public is exposed to any significant amounts of air-borne ENPs, although ENPs are present in certain consumer products. It is more likely that occupational exposures can be a factor in at least some settings.

6.8 Conclusions

The aim of the present article is to provide updated information on physico-chemical properties, sources and risk assessment of atmospheric nanoparticles. Apart from this information it also provides a survey of what is currently known about nanoparticles in the atmosphere, especially in terms of their formation and growth, number concentrations and chemical composition, and chemical, physical, and mechanical properties. Although combustion process in microenvironments is an important source of nanoparticles, the production of nanoparticles may cause hazardous biological effects. Therefore, detailed understanding of their sources, release interaction with environment and possible risk assessment would provide a basis for safer use of engineered nanoparticles with minimal or hazardous impact on environment. Uncertainties in conventional quantitative risk assessment typically relate to values of parameters in risk models. For many environmental contaminants, there is a lack of sufficient information about multiple components of the risk assessment framework. In such cases, the use of default assumptions and extrapolations to fill in the data gaps is a common practice. Nanoparticles risks, however, pose a new form of risk assessment challenge. Besides a lack of data, there is deep scientific uncertainty regarding every aspect of the risk assessment framework: (a) particle characteristics that may affect toxicity; (b) their fate and transport through the environment; (c) the routes of exposure and the metrics by which exposure ought to be measured; (d) the mechanisms of translocation to different parts of the body; and (e) the mechanisms of toxicity and disease. In each of these areas, there are multiple and competing models and hypotheses. These are not merely parametric uncertainties but uncertainties about the choice of the causal mechanisms themselves and the proper model variables to be used, i.e. structural uncertainties.

The present state of knowledge is unsatisfactory for a proper risk assessment of nanoparticles and improvements of the study qualities as well as an increased number of relevant studies are strongly recommended.

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