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Health hazards of ultrafine or nanoparticles in ambient air: Necessity for their standardization for air quality index (AQI)

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Abstract
Pollution level in the air, and hence the Air Quality Index (AQI) in all the countries is determined by the measurement of concentration of certain criteria pollutants, such as the Particulate Matter (PM_{10} and $PM_{2.5}$), CO, NH_3, NO, NO_2, SO_2, O_3, Pb, As, and Benzene etc. Of late, certain RSPM (Respiratory Suspended Particulate Matter), namely, $PM_{0.1}$ (ultrafine particles), which is the same as nanoparticles, have been found to cause much more damage to human health compared to any of the criteria pollutants. Unfortunately, no sufficient research work has been done till date to conclusively establish the extent of their damaging effects on the health of humans and other living beings. This important issue is highlighted in this paper and it is urged out that a systematic and detailed research work is carried out to formulate the standards of ultrafine or nanoparticles for linking with AQI.

Keywords: ultrafine particles, nanoparticles, atmospheric pollution, air quality index

1. Introduction

The World Health Organization (WHO) estimates that around two million people in the world die annually due to the effects of atmospheric pollution [1]. These estimates are based on epidemiological studies that showed associations between air pollution exposure, respiratory and cardiovascular illnesses, and deaths. Air pollution varies from place to place. Spending a day on the streets of New Delhi, for example, will have the same negative effect on one's respiratory tract as staying for 30 days in Melbourne. It should be noted, however, that people react differently to poor quality air, depending on their sensitivity, resistance developed at a particular place over a long period and medical history of the particular person.

In the next 20 years, nanotechnology will touch the life of nearly every person on the planet. The potential benefits are overwhelming and brain enhancing. Nanotechnology is being used for many everyday-life products such as in medicine, deodorants, sunscreens or socks. These are only a few examples of consumer products containing nano-sized particles. This "unique phenomena" make nanotechnology extremely important and give it the staying power because nano-enabled products often perform better than their non-nano counterparts do. Nonetheless, it is difficult to determine the distribution of nanoparticles in the environment and the risks to human health. Like many of the great advancements in earth's history, it is not without risk. However, there is uncertainty as to whether exposure to nanoparticles through dermal contact, inhalation, or ingestion can cause bodily injury. It is this potential toxicity that is a source of concern.

Total Suspended Particulate Matter (TSPM), particularly the crucial Respirable Suspended Particulate Matter (RSPM) in the ambient air includes PM_{10}, $PM_{2.5}$, $PM_{1.0}$, and $PM_{0.1}$ (ultrafine particles or nanoparticles). The main sources of outdoor PM pollution in developed and developing countries are commonly identified to be road traffic (including exhaust and non-exhaust emissions of vehicle combustion, tire wearing, and re-suspension), power generation plants, industries, agriculture, dust, forest fires, volcanoes, and domestic heating systems. While natural sources, which represent a consistent fraction of aerosols in many regions, contribute mainly on coarser particles, anthropogenic sources are well known for the generation of primary and secondary: fine, ultrafine or nanoscale particulates [2].

2. Characteristics of coarse, fine and ultrafine particles

Following Table distinguishes among coarse, fine and ultrafine particles [3]:

Table 1: Characteristics of coarse, fine and ultrafine particles

	Coarse Particles, $PM_{10-2.5}$ µm	**Fine Particles, $PM_{2.5-1.0}$ µm**	**Ultrafine Particles, $PM_{0.1}$ µm**
Mode	Coarse	Accumulation	Nucleation
Mode Formation and Sources	Break-up of solids and droplets; Erosion of land; Suspension of dust; Re-suspension of road debris (tire/brake wear); Ocean spray;	Condensation of atmospheric gases; Coagulation of ultrafine particles; Reactions of component gases of particles; Evaporation of water droplets	Nucleation and condensation of atmospheric gases; High temperature combustion (including vehicle exhausts);

	Ash (black smoke) from uncontrolled combustion ; Construction and demolition; Disturbance of surfaces (agriculture, mining, quarrying, unpaved roads); Biogenic emissions (pollen, fungal spores)	containing dissolved gases; Combustion of fossil and biomass fuels; Industrial processes (smelters, refineries, steel mills, mining).	
Composition	Organic and elemental carbon; Sulphates, Nitrates, Chlorides, Oxides of crustal elements; Sea salt; Plant and animal debris; Bacteria.	Organic and elemental carbon; Sulphates, Nitrates; Ammonium Metals; Organic compounds; Water; Bacteria; Viruses.	Organic and elemental carbon; Sulphates; Nitrates etc.; Metals; Organic compounds.
Physical characteristic of mode	Large mass	Large surface area	High particle number
Spatial/temporal variability	High	Low	Very high
Atmospheric life-time	Minutes to days	Days to weeks	Minutes to hours
Distance travelled	Usually <10’s kms	100’s-1000’s kms	Usually <1’s kms
Removal process	Gravitational deposition; Scavenging by rain.	Gravitational deposition; Formation of cloud droplets and rain out.	Coagulation, adsorption, condensation, diffusion to rain droplets.
Extent of physiological deposition	Upper airways (primary bronchi)	Lower airways (terminal bronchioles and alveoli)	Extra-pulmonary organs

3. More about ultrafine / nano-particles in ambient air

Ultrafine particles or nano-sized particles (that is, particles smaller than 100 nm) are a subgroup of the atmospheric particles. The first research studies used the term *ultrafine particles*. Nowadays this term is still being predominantly used in aerosol and environmental sciences. However, in 1990’s, the term *nanoparticles* became vastly popular as substitution of ultrafine particles and quickly became adopted in many fields, such as in medicine, material sciences and engineering. Due to very small mass of each ultrafine or nanoparticle, the concentration of these particles in air is most commonly measured and expressed in terms of number concentrations of particles per unit volume of air, like number of particles per cm^3 or parts per million (ppm) or parts per billion (ppb), in contrast to larger particles which are measured in terms of mass concentration, like $\mu g/m^3$. This is done because the small mass of ultrafine particles is eclipsed by the larger mass of fine and coarse particles [4].

Nanoparticles are not a new phenomenon. They are found in volcano ash, ocean spray, smoke, clouds, and clay after all. Depending on where it is, a cubic meter of air will contain hundreds of millions of nanoparticles, most of which are of natural origin or else – like diesel soot, for instance – are products of combustion processes. However, scientists warn that the idea of free born, manmade, and active particles is a risk that is in fact new. In addition, deliberately produced nanoparticles are often more bio persistent than soot or naturally occurring nanoparticles. The use of sprays designed to seal various types of surface could potentially result in inhalation of tiny droplets containing nanoparticles. Similarly, abrasion associated with the use of nanocomposites (tires, sporting equipment, etc.) could result in release of nanoparticles [5].

Ultrafine particles contribute by far the greatest number of particles to ambient PM, in what is called the “nucleation” mode. Inhaled ultrafine particles are small enough to be able to deposit in tissues outside of the lungs. Ultrafine particles are generated by high temperature combustion or formed from nucleation of atmospheric gases. It is hypothesized that ultrafine particles are dominated by primary anthropogenic combustion emissions in highly polluted urban settings and by nucleation of gases in remote sites. Organic and elemental carbon, trace metals, and sulphates are components of ultrafine particles from combustion sources. Sulphuric acid vapour and water vapour are the major nucleating gases. Ultrafine particles are quickly removed from the atmosphere (minutes to hours) via diffusion to surfaces or, coagulation, adsorption and condensing into fine particles. As a consequence, these particles are not transported far in ambient air and have great spatial and temporal variability. The ambient ultrafine particle concentration can be significantly higher near to traffic without similar increases in PM_{10} and $PM_{2.5}$ levels [6].

4. Sources of ultrafine or nanoparticles

The major natural sources of atmospheric nanoparticles are atmospheric formations, vegetation and sea sprays. Volcanic eruptions or forest fires also produce, though sporadically, a large number of atmospheric nanoparticles. The atmospheric formations of the particles include condensation of semi-volatile organic aerosols, photochemically induced nucleation, and/or nucleation through gas-to particle conversion. The formation of new nanoparticles is sometimes preceded by an increase in the atmospheric concentration of sulphuric acid [7]. Various studies have concluded that vehicle exhaust emissions represent a primary source of nanoparticle pollution in urban environments. The vehicle emissions depend on many factors such as type of engines, fuels, lubricating oil, after-treatment or driving conditions. Typically, particles emitted from diesel engines are in the size range 20–130 nm. Large part of nanoparticles is also produced by heavy-duty diesel vehicles (trucks, buses) that exhibit particle number emission factors one to two orders of magnitude larger than typical petrol cars. The industrial sources of atmospheric nanoparticles include power plants, incinerators, or various industrial processes such as smelting or welding, heating operations. Compared to vehicle exhaust emissions, their contribution to atmospheric nanoparticles is though much lower. The engineered nanoparticles are nowadays incorporated into many products of daily use (pharmaceuticals, lubricants, cosmetics, pharmaceuticals, fillers, catalysts, electronic devices or other domestic appliances. The widespread use of manufactured nanoparticles in consumer products may dramatically increase potential environmental, occupational, and public exposures to these particles that may result in adverse health effects if they are not appropriately controlled [8].

5. Chemical composition of ultrafine or nanoparticles

The composition of atmospheric nanoparticles is highly variable. The source and formations influence their chemical composition and nanoparticles include components such as inorganic compounds (sulphates, nitrates, ammonium, chloride, and trace metals), elemental and organic carbon, crystal materials, biological components (viruses), and volatile and semi volatile organic compounds. They can carry toxic compounds such as heavy metals, dioxins, hydrocarbons and other organic chemicals (some of which are potentially carcinogenic) adhered to their surfaces, which then increase their toxicity. Apart the source-specificity, composition of nanoparticles also depends on geographical and meteorological parameters, which in general lead to great differences in physicochemical properties among nanoparticles.

6. Harmful effects of some nanoparticles

As discussed before, ultrafine particles or nanoparticles are mostly composed of nitrates, sulphates, ammonium, and organic compounds as well as trace metals when formed from combustion processes. The cardiovascular toxicity of $PM_{0.1}$ may relate to the capacity of these particles to carry toxic compounds and the location of particle deposition. Compared to larger particles, $PM_{0.1}$ particles have a larger surface area per particle mass and hence a higher carrying capacity of potentially toxic substances. $PM_{0.1}$ is small enough to be able to translocate from the airways to the circulation and it has been found in the blood and various organs of experimental animals. The slightly coarser particulate matter (PM_{10}) is deposited in the nose, the throat, and the bronchial tubes. Fine particulate matter ($PM_{2.5}$) enters the bronchial tubes, and ultrafine particles travel to the deepest area of the lungs, where a significant part of them passes through the cell membranes of the alveoli (the millions of tiny sacs in our lungs where O_2 and CO_2 molecules are exchanged). Ultrafine particles enter the bloodstream, damage the inner walls of arteries, penetrate tissue in the cardiovascular system and potentially spread to other organs of the body such as the liver, the kidneys, the brain, and the heart [9]. At worst, ultrafine can contribute to deadly diseases like heart attacks, lung cancer, dementia, emphysema, edema and other serious disease, leading to premature death.

Tissue studies indicate that nanoparticles could damage DNA and lead to cancer [10]. Nanoparticles are small enough to penetrate cell membranes and defenses, yet they are large enough to cause trouble by interfering with normal cell processes. When nanoparticles find their way into cancer cells, they can wreak havoc. Yet very little is known about how they behave in the environment or how they interact with and affect humans. It has been observed both dose-dependent and time-dependent increases in DNA damage in breast cancer cells exposed to either aqueous colloidal silica or C-60 fullerenes. The DNA damage could potentially lead to mutations and ultimately increase the risk of cancer. What makes matters worse is the fact that so far, aside from preventing their release, there are no known ways to prevent the harmful effects of environmental nanoparticles.

Our knowledge of the potential harmful effects of nanomaterials is progressing more slowly than the technological developments. Inhaling certain nano-sized particles may result in local lung inflammation, allergic responses or harmful effects on genes. Some specific types of nano-fibers may cause similar reactions as asbestos including chronic inflammation. Additional concerns are related to internal exposure, as some particles may enter the bloodstream and accumulate in organs like the liver and spleen. Nanoparticulate matter is able to enter cells, which might in turn lead to direct and indirect genotoxic effects [11].

The characteristics of nanoparticles that are relevant for health effects are:

(i) Size: In addition to being able to cross cell membranes, reach the blood and various organs because of their very small size, nanoparticles of any material have a much greater surface to volume ratio (i.e. the surface area compared to the volume) than larger particles of that same material. Therefore, relatively more molecules of the chemical are present on the surface. This may be one of the reasons why the nanoparticles are generally more toxic than larger particles of the same composition.

(ii) Chemical composition and surface characteristics: The toxicity of nanoparticles depends on their chemical composition, but also on the composition of any chemicals adsorbed onto their surfaces. However, the surfaces of nanoparticles can be modified to make them less harmful to health.

(iii) Shape: Although there is little definitive evidence, the health effects of nanoparticles are likely to depend also on their shape. A significant example is nanotubes, which may be of a few nanometres in diameter but with a length that could be several micrometers. A recent study showed a high toxicity of carbon nanotubes which seemed to produce harmful effects by an entirely new mechanism, different from the normal model of toxic dusts.

Inhaled particulate matter can be deposited throughout the human respiratory tract, and an important fraction of inhaled nanoparticles deposit in the lungs. Nanoparticles can potentially move from the lungs to other organs such as the

brain, the liver, the spleen and possibly the foetus in pregnant women. Data on these pathways is extremely limited but the actual number of particles that move from one organ to another can be considerable, depending on exposure time. Even within the nanoscale, size is important and small nanoparticles have been shown to be more able to reach secondary organs than larger ones. Another potential route of inhaled nanoparticles within the body is the olfactory nerve; nanoparticles may cross the mucous membrane inside the nose and then reach the brain through the olfactory nerve. Out of three human studies, only one showed a passage of inhaled nanoparticles into the bloodstream.
The following diagram illustrates this pictorially [12]:

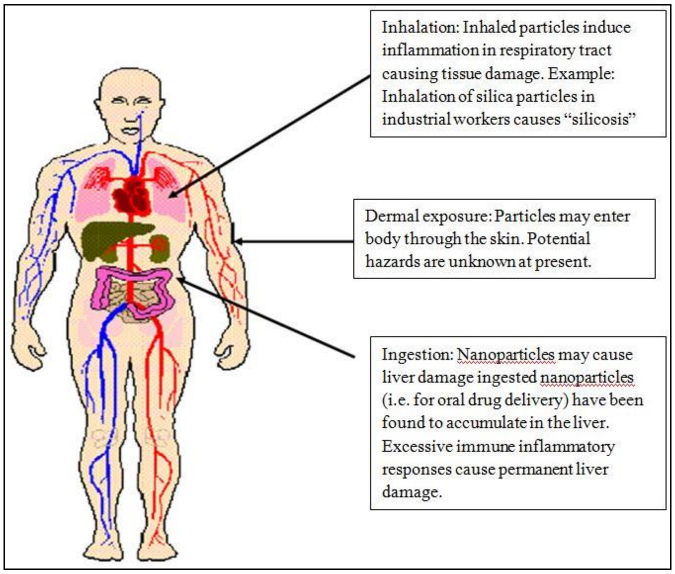

Fig 1

While nanomaterials present seemingly limitless possibilities, they bring with them new challenges to understanding, predicting, and managing potential safety and health risks. Nanomaterials have the greatest potential to enter the body through the respiratory system if they are airborne and in the form of respirable-sized particles (nanoparticles). They may also come into contact with the skin or be ingested. Studies in workers exposed to aerosols • of some manufactured or incidental microscopic (fine) and nanoscale (ultrafine) particles have reported adverse lung effects including lung function decrements and obstructive and fibrotic lung diseases [x12]. However, more research is needed to determine the key physical and chemical characteristics of nanoparticles that determine their hazard potential. The National Institute of Occupational Safety and Health (NIOSH) have recommended a REL (Recommended Exposure Limit) of 7 µg/m3 elemental carbon (EC) as an 8-hr TWA respirable mass airborne concentration [13].
There are almost no publications on the effects of engineered nanoparticles on animals and plants in the environment. However, a number studies have examined the uptake and effects of nanoparticles at a cellular level to evaluate their impact on humans; it can reasonably be assumed that the conclusions of these studies may be extrapolated to other species, but more research is needed to confirm this assumption. Moreover, careful examination and interpretation of existing data and careful planning of new research is required to establish the true impact of nanoparticles on the environment, and the differences with larger, conventional forms of the substances. Traditionally, doses are measured in terms of mass because the harmful effects of any substance depend on the mass of the substance to which the individual is exposed. However, for nanoparticles it is more reasonable to measure doses also in terms of number of particles and their surface area because these parameters further determine the interactions of nanoparticles with biological systems [14].

7. Urgent need for formulating standards of ultrafine particles (Nanoparticles) for defining air Quality Index (AQI)

Many governments are discussing how to regulate particle exposure levels of ultrafine particles since many sources (like combustion engines) generate higher amounts of $PM_{0.1}$. Epidemiological studies on ambient air pollution have not proved conclusively that ultrafine particles are more harmful than larger particles. Until date, there is no unanimity about the dosimetry of ultrafine particles including deposition patterns in the respiratory tract and, particularly, the biokinetic fate. Cardiovascular effects observed in epidemiological studies indicate an enhanced translocation of ultrafine particles from the respiratory epithelium towards circulation and subsequent target organs, such as heart, liver, and brain, eventually causing adverse effects on cardiac function and blood coagulation, as well as on functions of the central nervous system.
Unlike fine or coarse particles, the regulatory aspect of nanoparticles has not yet been addressed. No systemic, thorough and conclusive research has been conducted until date to study the harmful effects of ultrafine particles on the health of humans and other living beings. Consequently and unfortunately, no threshold limits have been identified for the ultrafine particles below which no damage to health is observed. The smaller the particles, the more dangerous they are to our health. Ultrafine particles (same as nanoparticles) can cause lung damage, cancer, and heart attacks, and stunt the physical development of humans particularly children.

8. Discussion and Conclusion

Although humans and other living beings have been exposed to ultrafine particles (nanoparticles) since many years, but this problem has assumed alarming proportion in the twenty first century. This is because of increase of anthropogenic activities, including vehicular exhaust, industrial processes and the unparalleled interest in the emerging nanotechnology. If unregulated, some of the nanoparticles in the ambient air will prove to be very harmful to humans and other living beings. The most vulnerable population facing the onslaught will be the children and elderly people. These nanoparticles may affect the brain, lungs, heart, liver etc and may cause an accelerated increase in the number of deaths in the world due to atmospheric pollution caused by some of the ultrafine particles (or nanoparticles). Unfortunately, no sufficient research work has been done till date to conclusively establish the extent of their damaging effects on the health of humans and other living beings. This has led to the absence of standards to be defined by WHO or any country, which links these standards to AQI. This important issue is highlighted in this paper. We strongly recommend a multidisciplinary approach including atmospheric scientists, nanomaterial engineers, epidemiologists, clinicians and toxicologists to investigate the sources, generation, physicochemical characteristics and potential harmful effects of nanoparticles. It is high time that standards are formulated for these ultrafine or nanoparticles along with those of existing criteria pollutants, after doing a though analysis of interaction of ultrafine particles (nanoparticles) with humans and other living beings before it is too late.

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