Chapter

Oxidative Stress Produced by Urban Atmospheric Nanoparticles

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Abstract

In urban areas, the diesel-fuelled and bio-fuelled vehicles represent the major sources of nanoparticles complemented by nanotechnology with different types of particles, in addition to natural and to other anthropogenic sources. The atmospheric nanoparticles differ in composition, size, shape or oxidant capacity, presenting a large variability that causes difficulties in their measurements and health impact identification. The oxidative stress can be initiated by atmospheric nanoparticles through different mechanisms: interaction between nanoparticles and tissue cells, cellular internalisation of nanoparticles, activation of signalling pathways, decrease of the cellular antioxidants, activation of the pro-inflammatory cascade, lipid peroxidation, activation of cellular signalling pathway that leads to apoptosis, etc. Ultrafine particles (<100 nm) represent ~80% of the total atmospheric particles and produce inflammation through oxidative stress mechanisms. The atmospheric nanoparticles can penetrate the skin and can be inhaled or ingested affecting different organs and leading to different diseases: neurodegeneration, thrombogenesis, atherosclerosis, asthma, lung cancer, heart arrest, etc.

Keywords: nanoparticles, particulate matter, urban atmosphere, reactive oxygen species, oxidative stress, atmospheric ultrafine particles, diesel exhaust particles, air pollution

1. Introduction

Urban atmosphere contains a mixture of nanoparticles with high variation in structure, number and chemical composition. This atmospheric nanoparticles' diversity is in close relationship with the natural or industrial sources, urban area location and meteorological conditions. In the troposphere, the nanoparticles can be found at all altitudes from sea level to 10 km, with concentrations that can largely vary between 10^2 and 10^5 particles/cm^3 [1]. Atmospheric nanoparticles are of different chemical structures (unstable molecules or ions, stable nuclei) with various shapes (most of them have irregular aspect) and with many origins. The human body can be affected by nanoparticles exposure, because these particles penetrate easily through skin, respiratory system, or digestive tract. The atmospheric nanoparticles can produce oxidative stress through different mechanisms, from the reactive oxygen species (ROS) synthesis till the decreasing of body's antioxidant capacity [2].

This chapter will use the terms nanoparticles (NPs) or particulate matter ($PM_{0.1}$) for particles with sizes lower than 100 nm (lower than 0.1 μm).

2. Atmospheric nanoparticles

Earth's atmosphere contains particles with sizes between few nanometres and hundreds micrometres. They are produced naturally or by anthropogenic emissions, in concentrations that vary greatly, in accordance with the geographical areas and meteorological conditions. Naturally, the atmospheric particles can be produced from many sources: sea salt aerosols produced by breaking waves [3], cosmic dust [4], atmospheric formation of NPs from atmospheric particles (for example, photochemically induced nucleation) [5], forest's aerosols [6], volcanic eruptions, or forest fires. Anthropogenic emissions that produce atmospheric particles are represented by: vehicles, industry, power plants, incinerators, nanotechnology [7], fossil fuel exploitation, mining techniques, stone quarries [8], etc. Over the continents, close to the ground, the air contains 103–105 nanoparticles/cm^3, most of them chemically generated through coagulation or condensation [9].

Atmospheric particles are classified according to their diameter into: supercoarse, coarse, fine and ultrafine particles. Supercoarse particles (>10,000 nm diameter) do not enter the respiratory system. The coarse particles (diameter 2500–10,000 nm), represented by pollen, spores, sea salt aerosols, or by the particles generated through wind erosion, deposit on the ground within few hours after their production but can also enter the upper airways of the human respiratory tract, from where they can be eliminated back into the atmosphere by coughing, or they can be ingested by swallowing [10]. The fine particles (100–2500 nm diameter) produced naturally (through nuclei-mode particles coagulation or through vapour molecules condensation on particles surfaces) but mostly through anthropogenic processes (vehicles or industry emissions) [11], can enter the respiratory tract till the alveoli level. Because the fine particles have small diameters, the gravitational forces affect them only partially and they can persist in the atmosphere for days or weeks, being also able to travel over long distances [12]. Ultrafine particles (<100 nm diameter), also named nanoparticles, are produced through condensation of vapour molecules and form nuclei, instable particles that persist in atmosphere only for a short time (few minutes till few hours), close to their source, with rapid changes in number distribution. The inhaled NPs can pass through the respiratory membrane, entering the blood and travelling through the circulatory and lymphatic systems to the body's organs [13].

The atmospheric particle concentration is influenced by meteorological conditions. Wind speed improves the atmospheric air, especially if it is higher than 6 m/s. The temperature influences the air quality: a very high or a very low temperature is correlated with increased concentration of atmospheric particles because usually, these extreme temperatures occur synchronous with high atmospheric pressure that blocks the air motion. The high cloudiness is usually accompanied by low atmospheric pressure and high-speed winds, conditions that reduce the particles concentration in the atmosphere. The association of thin planetary boundary layer (peplosphere, the lower part of the troposphere) with high atmospheric pressure can block the particle motions, leading to an increased density of noxious substances in the air [14]. The urban areas located in valleys present atmosphere with reduced particle dispersion and have winds of low speed, conditions that lead to increased concentration of particles [15]. In the urban zones located in arid areas, the strong wind increases the particulate matter concentration [16].

2.1 Sources, chemical composition and morphological aspects of atmospheric nanoparticles

The diversity of atmospheric nanoparticles, as a result of highly variable sources and chemical composition, can explain the different effects on human body. Inorganic compounds (nitrates, ammonium, sulphates, trace metals) and organic compounds (hopanes from engine oils, organic acids) can attach noxious substances and can lead to severe diseases. The industrial zones release the atmosphere nanoparticles with high quantities of Fe, K (from biomass burning), or Ca (found in oil as additive) [17–19].

In urban atmosphere, different types of metallic NPs were identified, from which 50% contain two or more metals in their composition [20]. The most common metals are Fe, Ca, Al, Mg, Zn, Na, and they have many sources, from vehicles emission to industrial processes [21]. The principal source for metallic nanoparticles is represented by the vehicles through lubricating oil additives [22], diesel fuel additives [23], brake mechanism (releases 26–44% $PM_{0.1}$ because of metal volatilisation by heating) [24] and tyre dust (emits NPs of 15–50 nm diameter) [25]. Metallic NPs can also be produced through the wood combustion [26] and in port areas, by marine diesel engines [27]. Nanoparticles emitted by diesel engines contain a core made from solid elemental carbon and a layer of volatile organic carbon. They are of 10–50 nm diameter and can attach water-soluble ions, traces of elements from lubricants, or from engine functional abrasion [28].

Decamethylcyclopentasiloxane (D5), a volatile cyclic siloxane, found in personal care products is released in atmosphere in big quantities, with high concentrations during winter (~1 ng/m^3) and low concentrations during summer (~0.3 ng/m^3). D5 is transported in the atmosphere over long distances, but with seasonal variation, depending on the availability of OH radical ($OH^{\cdot}$) in the air, an oxygen species with which it reacts very quickly. Even if D5 can persist for almost 10 days in the atmosphere, it reaches the ground very rarely [29].

Silicon, a common compound of atmospheric nanoparticles, is detected in high concentrations in geographical areas with anthropogenic sources, with maximum levels during the daytime because Si-NPs production occurs through photochemical reactions. The oxidation of D5 leads to the development of Si nanoparticles in urban areas [30].

Morphological aspects of atmospheric nanoparticles differ in concordance with the emitting sources. The NPs identified in rail subways have specific chemical composition and specific morphology. Fe-NPs have irregular aspects: flake-like, botryoidal, crystal-like, or aggregated particles and most of them contain carbon. Calcium and silicon are often identified in the platform environment. In the subway's air, there also exist high concentrations of other metals (Zn, Ti, Sb) and traces of Al, K, Na, Mg, Cr, Co, S and Cl. Most of the inhaled Fe-NPs have the flake aspect, with different incorporated compounds [31].

2.2 Production of urban atmospheric nanoparticles

Ultrafine particles are produced through nucleation (vapour substances condense around the particles). An increase in atmospheric concentration of sulphuric acid leads, within 1–2 h, to an increase in particle number [32], with a reduced particle growth rate [33]. Sulphuric acid is considered an important factor for aerosol nucleation that leads to production of 2–3 nm NPs. Organic vapours can also produce nanoparticles with dimension that depend on the particle acidity, relative humidity and mechanisms of synthesis. Amines can lead to 4 nm NPs production, while organic carbonyls (aldehydes, α-dicarbonyls) can develop 4–6 nm particles [34].

Atmospheric nanoparticles can also be produced through evaporation of volatile compounds of larger particles [35].

The ultrafine particles with sizes between 1.5 and 2 nm form new larger particles through homogenous nucleation, process that occurs rapidly and leads to NPs dilution near the emission source [36]. Dry or wet depositions of particulate matter to the surfaces are important only for particles larger than 100 nm [37]. Most of the atmospheric NPs are too small to form cloud droplets that can be eliminated from the air by rain. The rainfall rate and the rain duration are important factors in NPs removing from the air, by production of larger particles that can be wet-deposited on surfaces [38].

There exist big differences in nanoparticles concentration measured in rural areas (2.6×10^3 to 4.8×10^3 particles/cm^3), in urban environments (42.1×10^3 to 48.2×10^3 particles/cm^3) [39] and in road tunnels (167.7×10^3 particles/cm^3) [40]. The rate of nanoparticles production is ~10^2 NPs/cm^3/s in urban areas and 10^4 to 10^5 NPs/cm^3/second in industrial and costal zones [41].

In urban atmosphere, the anthropogenic emissions represent the major sources of NPs, the vehicle emissions producing ~86% of the total atmospheric ultrafine particles [42]. There are many factors that can affect the NPs number concentration after vehicle emissions and among them, dilution is the most important event that depends on traffic conditions and has a duration of about 1 s [43]. Petrol (gasoline)-fuelled vehicles emit a low number of nanoparticles with sizes between 20 and 60 nm, while diesel-fuelled vehicles emit the most of atmospheric NPs but with a higher diameter, 20–130 nm [44]. An important factor for NPs emitted in the atmosphere is the driving manner: the petrol-fuelled vehicles driven at high speed (~120 km/h) and acceleration of these cars lead to emission of NPs in a similar number with the NPs number recorded at the diesel-fuelled cars emission [45]. The particles emitted by the vehicles are classified, according to their formation, into two groups: primary and secondary. The primary particles are released directly in the atmosphere like adsorbed or condensed hydrocarbons, sulphur compounds or metallic ash and their size is between 30 and 500 nm. The secondary particles are produced in the atmosphere from emitted hot gases that cool and condensate as nanoparticles with diameter lower than 30 nm, consisting of hydrated sulphuric acid and hydrocarbons [46].

Another factor that increases the particles concentration in the atmosphere is represented by the interaction between road and tyres [47].

In urban atmosphere, the industrial sources also contribute to NPs production, but only with 2%.

Nanotechnology developed new types of nanoparticles that are different in comparison with those found in the atmosphere, and even if these engineered NPs are incorporated in different products, they can escape in the environment, increasing the concentration of atmospheric ultrafine particles [48].

Cosmic dust enters the Earth atmosphere with 40,000 tons of particles/year. The cosmic particulate matter with low-velocity, mostly from asteroids and comets, can reach the ground [49, 50]. In the atmosphere, most of the cosmic particles are destroyed but some of $PM_{0.1}$ are vaporised and then recondensed into individual particles, being a source of iron nanoparticles [51].

2.3 Atmospheric nanoparticles in different urban areas

In urban atmosphere, the complex and turbulent mixing mechanisms influence the NPs flow around or over the buildings and streets.

The highest concentration of particulate matter is recorded in traffic intersections, but it is also increased in street canyons and on the roadsides, in comparison with the urban peripheral areas [52].

Within the street canyons, the nanoparticles' concentration depends on: traffic, atmospheric conditions (wind flow velocity, air temperature) [53, 54], street dimensions (large or narrow), street style (trees, street squares) and buildings' type (small or tall, balconies, walls roughness) [55].

In traffic intersection atmosphere, the concentration of nanoparticles emitted by cars depends on driving conditions. It is maximum during deceleration, it presents increased values during acceleration or cruising, and it is minimum during idling. The stop-and-go driving at the roads intersection produces NPs that can be identified in an area between 120 and 379 m, depending on intersection type [56].

The road tunnels environment has specific characteristics due to the "piston effect" produced by the traffic direction that generates a turbulent flow of mixed NPs-vehicle generated [57]. These specific properties of road tunnel air (that are not influenced by meteorological conditions), and the presence of high concentrations of precursor molecules provide the appropriate environment for nanoparticles formation (through nucleation) that are then transformed into larger molecules (through coagulation) [58].

In underground car park, the particulate matter concentration is higher than in opened urban area, with values that vary according to the traffic and dust presence on the ground. The entrance air in the park contains lesser concentrations of particulate matter than the exit air (acceleration, disc brake friction, dust re-suspension). The elements identified in underground car park environment are: Fe and Mn (the most abundant and related to dust re-suspension) and Zn and Cu (related to brake abrasion and tyre wear) [59].

On rail subways, the nanoparticles are made up of Fe, and their concentration, number and size are dependent on the train speed, pressure exerted on the rails, material of rails and wheels, lubricants used to reduce the wear, and on the temperature generated by the rail-wheel contact [60]. The nanoparticles concentrations are much higher than those above the ground [61]. Most of the NPs consist of Fe structures that are unique to the subways air, and their dimensions are very small [62].

3. Urban atmospheric nanoparticles in the human body: penetration, storage and elimination

The short-term exposure to atmospheric NPs exacerbates the chronic pulmonary and cardiovascular diseases and the long-term or repeated exposure can lead to death [63].

The respiratory system, digestive tract and skin are passed by the atmospheric nanoparticles [64], process that leads to oxidative stress, inflammation, or other pathological effects. The noxious effects of NPs depend on their size, chemical structure, or shape [65]. The skin penetration of atmospheric nanoparticles is realised transcellular (NPs <75 nm), intercellular, through the hair follicles, sweat and sebaceous glands [66]. Inside the dermal fibroblasts, nanoparticles generate genotoxic effects [67] and in the keratinocytes produce oxidative stress with DNA damages [68]. The structure of hair cuticula and of follicular canal permits mostly the passage of fine particles (~300–600 nm) [69]. The respiratory system is another entering route for nanoparticles through inhalation or through the wall of air passageways [70].

The storage of atmospheric nanoparticles is realised in many organs: lymph nodes, spleen, lungs, liver, brain, bladder, cardiovascular system, bone marrow, etc. [71].

The penetrated nanoparticles can be eliminated from the body through the faeces and urine, in quantities that are related to the NPs properties [72].

4. Oxidative stress produced by urban atmospheric nanoparticles

Space weather affects the human body, initiating different pathological mechanisms [73]. High-energy cosmic radiation may interact with atoms, compresses them, and pushes the electrons into the nucleus, leading to the transformation of protons into neutrons, with electron neutrinos release [74]. In the body's tissues with high amount of H^+, neutrons can produce the recoil protons, subatomic particles that can destroy the cells [75]. Neutrons can be carried inside the human body by the atmospheric NPs [76], where they can produce oxidative stress that damages the tissues.

Decamethylcyclopentasiloxane (D5), a highly volatile substance, affects the human body only after long-term exposures, leading to the decreased secretion of prolactin from the pituitary gland because of its indirect dopamine-like effects, or to the lung inflammation [77]. The respiratory system is affected by most of the air nanoparticles, the oxidative stress and sensitisation being the common mechanisms that initiate or exacerbate the asthma [78]. Oxidative stress promotes DNA alterations and other cellular disturbances that may lead to lung cancer [79].

The nanoparticles emitted by diesel engines have chemical structures (elemental carbon with absorbed organic compounds, metals, nitrates, sulphate, etc.) that can cause inflammation and oxidative stress in the lungs [80] but they can also pass into the brain [81] and initiate pathological processes in the central nervous system [82]. Inhaled diesel NPs not only affect the CNS through direct mechanisms because they can cross the blood-brain barrier, but also through indirect processes that involve the cytokines released from the areas where respiratory and cardiovascular inflammation develop. Microglia activation, oxidative stress, vessels microlesions and neurotoxic effect of cytokines stimulate the neurons degeneration [83]. Organic matter combustion or frictional heating of brake pads release in urban atmosphere nanoparticles of magnetite a ferromagnetic compound that contains Fe^{2+} and Fe^{3+} [84, 85]. They can enter the human brain through olfactory nerve and produce oxidative stress that can initiate neurodegeneration, process responsible for Alzheimer disease [86]. Al-NPs cause oxidative stress in brain vessels' endothelial cells and alter the expression of tight-junction proteins [87]. Nanoparticles can deposit in other parts of the brain (hypothalamus, cerebellum, frontal cortex, brain stem, etc.) because of their structural characteristics that permit the passage at the synaptic junctions and through blood-brain barrier [88], leading to neuroinflammation, similar to that identified in Alzheimer disease [89]. Diesel NPs can pass rapidly into the circulatory system. They produce endothelial dysfunction at the microcirculation level, accumulate at inflammation sites, especially in atherosclerotic plaques [90], and are able to pass into the foetal circulation through placenta barrier, being considered teratogen factors [91]. Inhalation of diesel-emitted NPs stimulates the platelet aggregation [92] and may trigger thrombogenesis. They stimulate lipid peroxidation in the tissues (small intestine, liver, etc.) and in the plasma, the oxidation of HDL altering the protective role of this lipoprotein [93]. The inflammation, increased oxidative stress [94], vasoconstriction, or endothelium dysfunctions promoted by the NPs prolonged exposure can lead to atherosclerosis [95]. The exposure to atmospheric NPs initiates the mechanisms that lead to myocardial ischemia in patients with coronary diseases [96]. Atmospheric $PM_{0.1}$ affects the blood flow into the vessels, decreasing the blood pressure [97] or increasing it [98], depending on the particulate matter and on the patient status. Nanoparticles can pass inside the cells and alter the functions of cellular proteins, cellular organelles and DNA [99]. Diesel nanoparticles damage the DNA through different mechanisms: direct attack on DNA, DNA oxidation, or inflammatory processes that generate excessive ROS with genotoxic effects [100]. The nanoparticles emitted by diesel engines or by other pollutant sources are able to initiate protein citrullination that leads to autoimmune diseases like collagen-induced arthritis [101].

Among the urban atmosphere nanoparticles, many are photochemically active (SiO_2, ZnO, TiO_2) and can produce exited electrons that can be transferred to the oxygen molecule, leading to superoxide radical ($O_2^{\cdot -}$) [102]. Most of the NPs contain Fe, Ca, Si, Zn, Cr, components that trigger the oxidative stress through Fenton or Haber-Weiss-type reactions, with production of $O_2^{\cdot -}$, $OH^{\cdot}$ and $1O_2^{\cdot}$ (singlet oxygen) [103]. NPs can alter the function of proteins [104] and lipids. Ti-NPs have affinity for lipids, being accumulated in cellular membrane in big quantities that rupture the membrane. Inside the cell membrane, Ti-NPs are covered by lipids, proteins and tissue factor and move away from the initial location. Internalisation of the covered Ti-NPs stimulates the lysosomes enzymes to degrade the nanoparticles' coat, letting the nanoparticles' active surface to attack the lysosomal membrane, leading in the end to the death of the cell [105]. Like Ti-NPs, also Zn-NPs and Ce-NPs can be stored in the cell membrane or in the organelles and can initiate oxidative stress [106].

The presence of Fe-NPs, especially in the subway environment, stimulates the oxidative stress and the DNA lesions [107]. Fe-NPs penetrate easily inside the cells, target the endoplasmic reticulum and mitochondria and lead to ROS synthesis [108]. Ca-NPs are transported rapidly into the circulatory system and can bind plasma proteins [109]. Ultrafine particles can pass easily into the cell increasing the cellular calcium concentration that stimulates the release of cytokines [110], inflammatory molecules that stimulate the oxidative stress [111].

The same effects of NPs were seen on erythrocytes: easy penetration of ultrafine particles, increased calcium concentration inside the cytoplasm, oxidative stress, processes that lead to haemolysis [112]. $PM_{0.1}$ exposure has effects also on white blood cells, producing an increase of monocytes concentration [113].

5. Conclusions

Urban atmospheric nanoparticles penetrate the human body and stimulate the oxidative stress in many organs leading to acute or chronic diseases, according to the time of exposure. The smaller nanoparticles penetrate easier inside the tissue cells, and their effects depend on the chemical composition, dimension, morphology, and on the reactive sites that are present on their surface. Urban atmosphere contains a complex mixture of different nanoparticles that are characteristic to specific urban locations. Prolonged exposure to high concentration of NPs in urban or industrial areas can lead to severe diseases or even death. New researches are required to complete the general view of the complex urban atmosphere.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this chapter.

Abbreviations

ROS	reactive oxygen species
NPs	nanoparticles; particles less than 100 nm in diameter
$PM_{0.1}$	particulate matter less than 0.1 μm in diameter
D5	decamethylcyclopentasiloxane
CNS	central nervous system
HDL	high-density lipoprotein

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